**Filière Conservation-restauration**
Orientation objets archéologiques et ethnographiques

haute école neuchâtel berne jura arts appliqués la chaux-de-fonds

# Testing corrosion inhibitors for the treatment of marine iron / waterlogged wood composite artifacts in polyethylene glycol solutions

Mémoire présenté par :

Sangouard Elsa

Pour l'obtention du diplôme

des Hautes écoles spécialisées de Suisse occidentale

29/08/08

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# *Acknowledgments*

**Many thanks go to:**

My mentor:

Christian Degrigny, Professor-Researcher at the HEAA Arc (La Chaux-de-Fonds, Switzerland) and coordinator of the ICOM-CC Metal Working group, for his assistance and support over the year as well as for his thorough review.

My supervisor:

Eric Nordgren, Senior Conservator at TMM® (Newport News, Virginia, USA), for his guidance, support, patience, and significant readings.

As well as:

Marcie Renner, Chief Conservator at TMM®, for welcoming me at the Batten Conservation Complex, providing me access to all the infrastructure and materials required for this study and for her support throughout the year.

Dr. Desmond C. Cook, physics professor at the Old Dominion University (Norfolk, Virginia), for welcoming me to the laboratory, providing me access to the potentiostat, as well as X-Ray Diffraction (XRD) analyses and help with many questions.

**To the following institutions:**

The Old Dominion University (Norfolk, Virginia), The National Oceanic and Atmospheric Administration (NOAA) and The Mariner's Museum® (Newport News, Virginia) for equipment, materials, welcoming me and for financial funding.

**Special thanks for their help to:**

Erin Secord, Conservator at TMM®, for her remarkable support throughout the year, for her scientific and literary assistance.

Susanne Grieve, Conservator at TMM®, for her support, input in providing analogue materials as well as for sharing her experience with waterlogged organic conservation.

David Krop, Conservation Project Manager at TMM®, for encouragement as well as his editing advice.

Stéphanie Hollner, PhD Student, Laboratoire de Recherche des Monuments Historiques (LRMH, Champs-sur-Marne, France), for welcoming me at the LRMH and for sharing her knowledge about carboxylates, as well as remaining readily available for questions throughout the year.

Elodie Guilminot, Conservation Scientist at Arc'Antique (Nantes, France), for her advices and help over the year, notably about Hostacor IT®.
Thanks as well to Tina Gutshall, Assistant Conservator, Gary Paden, Artifacts Handler and Michael Saul, Technician at TMM®, for welcoming me and helping me over the year.
And also to Chief Warrant Officer 2nd Class Kasztelan and Petty Officer 1st Class Jesse Hamilton for their help in looking for analogue material.

**My school and my professors:**
Valentin Boissonnas, Metal conservation professor at the HEAA Arc, for his encouragements about this study. As well as Nathalie Ducatel, Director, HEAA Arc, Christian Binet, Tobias Schenkel, Alexis Domjan and Julita Beck for their support during my education.

I owe thanks to the following people for their individual support throughout the year during this project:
Alain Sangouard; Mathias Sangouard; Aude-Laurence Pfister; Noemie Van de Peol; Héloïsa Munoz; Claire Bancel; Loubna and Masson Hoggard; Ubie and Damamas Reed; Anushkush and Dreadopher Garrett; Stefanie Bruhin; Marie Ivanco and of course Mr. Reed.

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# *Abstract*

Non-separable iron/wood composite artifacts recovered from a marine environment are complex objects and require a good knowledge of conservation issues related to both materials before planning treatments. Their conservation involves compromises but intends to first treat the most fragile component while preventing alteration of the associated materials.

A particular issue for such treatments is the impregnation of the wooden parts, since the polyethylene glycol (PEG) commonly used to consolidate waterlogged wood is slightly acidic and aggressive to metal. An alternative to PEG can be the use of solvent based treatments but such options cannot be applied to large artifacts for safety reasons. The addition of corrosion inhibitors to PEG solutions is another possibility that has been studied for thirty years. The most well-documented corrosion inhibitor used for this purpose is Hostacor IT®. Over time, conservation professionals noticed several drawbacks of this chemical. Therefore, testing other corrosion inhibitors in PEG solution was found to be a worthwhile pursuit within the framework of this diploma.

A solution of 1% (v/v) Hostacor IT® was employed as a reference solution to enable comparisons with other chemicals. The corrosion inhibitors chosen had to be readily available, independent of a patent, easy to prepare, easy to use, affordable and safe. New research on corrosion inhibitors for cultural heritage properties highlights the performance of the "eco-friendly" carboxylate family of chemicals. Two corrosion inhibitor mixtures, designed for iron, were chosen from among the carboxylates: the sodium decanoate (at 0.05M) and the carboxylatation solution. A third chemical, sodium nitrite (at 100ppm), was included in these trials because a recent study, performed by the Mariners' Museum® (TMM®, Newport News, Virginia), demonstrated that sodium nitrite could be used as an alternative to alkaline solutions as a storage medium for large metallic artifacts.

The methodology followed to assess the effectiveness of these corrosion inhibitors in PEG solution was to simulate the treatment of a non-separable marine iron/wood composite object by using iron based samples. In order to replicate real artifacts as best as possible, naturally corroded iron based coupons were tested in parallel to bare metal samples. The metal tested was carbon steel.

To compare the performances of the chemicals on the metal samples, their corrosion potential ("$E_{corr}$") was monitored, in the solutions, over time. Two complementary accelerated aging tests were performed on the treated samples afterwards. The first aging method simulated the behavior of the metal in contact with high concentrated PEG solution. This represents a post-impregnation condition of a composite object. This behavior was determined with voltammetric plots measurements. The second method exposed the samples to 30 wet / dry cycles in a humidity chamber to simulate an uncontrolled museum environment.

The first noteworthy result of this project is that none of the corrosion inhibitors tested, Hostacor IT® included, are effective at preventing corrosion in a subsequent 20% (v/v) PEG impregnation treatment. This means that an iron/wood composite artifact first immersed in a corrosion inhibitive solution, e.g. as storage, cannot afterwards be immersed in a "simple" PEG solution without corrosion of the iron parts.

Considering the corrosion inhibitors in 20% (v/v) PEG solution, the carboxylatation solution did not appeared well suited to iron/wood composites due to its low pH that would be harmful to the wooden components.

The sodium decanoate showed promising results on bare carbon steel but has been shown, in previous studies, to be ineffective on corroded iron and is therefore not appropriate for iron/waterlogged wood composites.

The sodium nitrite solution showed good results, but its compatibility with PEG may not be assured because it tends to decrease the pH of the solution. In the case of iron/wood composite treatments, this could cause damage to the wooden part from high acidity and less protection for the metal.

Among these trials, Hostacor IT® remained the most appropriate corrosion inhibitor for the treatment of iron/waterlogged wood in PEG solution due to its neutral pH and its ability to passivate corroded steel. It is therefore unfortunate that this chemical is not readily available for purchase anymore. This, among other drawbacks of Hostacor IT®, should encourage conservation scientists to develop chemicals other than Hostacor IT® that are similarly effective.

## *Résumé*

Les composites fer/bois gorgés d'eau indissociables, issus du milieu marin, sont des objets complexes qui nécessitent une bonne connaissance des problèmes de conservation de chacun des matériaux en présence. Leur traitement implique des compromis mais vise souvent à la sauvegarde de chacun des matériaux tout en évitant l'altération du composant le plus fragile.

Un problème majeur de ce type d'objet est l'imprégnation de la partie organique puisque le polyéthylène glycol (PEG), couramment employé pour la consolidation des bois gorgés d'eau, est légèrement acide et, de ce fait, corrode le métal. Une alternative au PEG peut être l'utilisation de traitement à base de solvants. Cependant, pour des questions de sécurité, ce type de d'imprégnation n'est pas adapté aux objets de grandes tailles. Une autre possibilité consiste à ajouter un inhibiteur de corrosion au PEG durant le traitement de la partie organique. Cette option a été étudiée depuis une trentaine d'années. A ce jour, l'inhibiteur de corrosion le mieux connu est l'Hostacor IT®. Toutefois, l'expérience des professionnels de la conservation-restauration ayant mis en évidence un certain nombre de reserves quant à l'emploi de ce produit, il nous a semblé intéressant de tester l'efficacité d'autres inhibiteurs de corrosion en milieu PEG.

Une solution de 1%(v/v) d'Hostacor IT® a été employée pour ce projet, en tant que solution de référence. Les inhibiteurs de corrosion choisis devaient être : facilement disponibles, non brevetés, de préparation et d'usage facile, non toxiques et peu onéreux. De récentes recherches ont démontré l'efficacité de la famille des carboxylates, inhibiteurs de corrosion respectueux de l'environnement. Deux produits adaptés au fer ont été retenus parmi eux : le décanoate de sodium (à 0,05M) et la solution dite « de carboxylatation ». Un troisième produit, le nitrite de sodium (à 100ppm), a également été sélectionné. Ce dernier a montré des résultats prometteurs lors de recherches menées au Mariners' Museum® (TMM®, Newport News, Virginie) considérant des alternatives possibles aux solutions caustiques de stockage de grands objets métalliques.

La méthodologie retenue pour étudier l'efficacité de ces produits en milieu PEG a consisté à simuler le traitement de composites fer/bois gorgé d'eau sur des coupons de métal. Afin de rester aussi proche que possible des conditions réelles des artéfacts, des échantillons corrodés naturellement ont été comparés à des coupons non corrodés. Le métal testé était de l'acier.

Dans un premier temps l'efficacité des différentes solutions a été comparée par méthode électrochimique. Le potentiel de corrosion ("$E_{corr}$") des échantillons a été mesuré en fonction du temps. Ils ont ensuite été soumis à deux tests complémentaires de vieillissement accéléré. Le premier test simulait le comportement du métal au contact d'une solution fortement concentrée en PEG afin de représenter des conditions post-imprégnation d'un objet composite. Des mesures voltamétriques ont été employées pour cela. Le deuxième test a consisté à exposer les échantillons dans une chambre humide, à trente cycles alternant une atmosphère humide/sèche, afin de simuler l'environnement mal contrôlé d'un musée.

Le premier résultat intéressant de cette étude est qu'aucun des inhibiteurs de corrosion employé ici, Hostacor IT® inclus, ne prévient efficacement de la corrosion lors d'un traitement ultérieur dans 20% (v/v) PEG. Cela signifie qu'un composite metal/bois stocké dans une solution inhibitrice ne pourra pas, par la suite, être immergé dans une solution de PEG "simple" sans que cela implique la corrosion des éléments ferreux.

Concernant les inhibiteurs de corrosion associés à 20% (v/v) de PEG, la solution de carboxylatation est à déconseiller pour les composites fer/bois du fait de son pH bas qui endommagerait les parties organiques.

Le décanaote de sodium a montré des résultats intéressants sur l'acier non corrodé, mais est sans effet sur les produits de corrosion, comme l'ont révélé des études antérieures. Pour cette raison, cette solution est inadaptée aux composites fer/bois.

Le nitrite de sodium semble prometteur, mais sa compatibilité avec le PEG n'est pas garantie puisque le pH de la solution tend à diminuer en présence de PEG. Cela pourrait, dans le cas des composites fer/bois, abimer le bois et diminuer la protection du métal.

De tous les inhibiteurs de corrosion, l'Hostacor IT® reste le mieux adapté au traitement de composites fer/ bois gorgés d'eau en solution de PEG. Ceci est le fait, combiné, du pH neutre de la solution et de la capacité d'Hostacor IT® à passiver des surfaces corrodées. Cependant, parmi les

limites de ce produit, il s'avère notamment que celui-ci n'est plus commercialisé. Ce constat devrait encourager les scientifiques à développer d'autres inhibiteurs de corrosion d'efficacité comparable à l'Hostacor IT®.

## *Zusammenfassung*

Nicht trennbare Eisen/Holz ,aus einer Meeresumwelt geborgene, von Wasser durchtränkte Artefakte sind komplexe Objekte und erfordern vor jeder Behandlung präzise Kenntnisse bezüglich der Erhaltungsprobleme im Zusammenhang mit beiden Materialien. Ihre Konservierung erfordert Kompromisse : sie zielt darauf ab, alle Materialien zu konservieren , ohne dabei die fragilsten Komponente zu beschädigen.

Ein besonderes Problem bei einem solchen Verfahren stellt die Imprägnierung der Holzteile dar, da das meistens zur Konsolidierung des nassen Holzes verwendete Polyethylenglykol (PEG) leicht sauer ist und das Metall attackiert. Eine Alternative zur PEG wäre eine auf Lösungsmitteln basierendes Verfahren, aber eine solche Option ist bei großen Artefakten aus Sicherheitsgründen nicht praktisch möglich. Die Addierung von Korrosionsinhibitoren zu PEG-Lösungen ist eine weitere Möglichkeit, die seit etwa dreißig Jahren studiert worden ist. Der am besten dokumentierte, zu diesem Zweck verwendete Korrosionshemmstoff ist Hostacor IT®. Im Laufe der Zeit hat sich aber diese Chemikalie in mancher Hinsicht als problematisch erwiesen. Aus diesen Gründen haben wir uns in dieser Studie vorgenommen, die Wirkung weiterer Korrosionsinhibitoren in einer PEG-Lösung bei diesem Anwendungsbereich zu untersuchen.

Eine Lösung von 1% (v/v) Hostacor IT® wurde als Referenz-Lösung benutzt, um Vergleiche mit anderen Chemikalien zu ermöglichen. Bei der Wahl der Korrosionsinhibitoren wurde auf Folgendes geachtet : sie sollten leicht verfügbar, unabhängig von einem Patent, leicht vorzubereiten, leicht zu benutzen, billig und ungefährlich sein. Neue Forschungen über Korrosionsinhibitoren für Restaurierungs, bzw Konservierungszwecke, heben besonders wirksame Eigenschaften der umweltfreundlichen carboxylat-Gruppe hervor. Zwei Kombinationen von Korrosionshemmstoffe einsetzbar mit Eisen, wurden aus dem Gruppe der carboxylate ausgewählt: die Natrium decanoate (at 0.05M) und die sogenannte « Carboxylatationslösung ». Eine dritte Chemikalie, Natrium-Nitrit (100ppm), wurde ebenfalls bei diesen Experimenten in Betracht gezogen, weil eine neue Studie, durchgeführt vom Mariners' Museum® (TMM®, Newport News, Virginia), bewiesen hat, dass Natrium-Nitrit als eine Alternative zu Laugen bei der Speicherung großer metallischer Artefakte verwendet werden konnte.

Die Methodik zur Einschätzung der Wirksamkeit dieser Korrosionsinhibitoren in PEG-Lösung bestand darin, die Behandlung eines nicht-trennbaren marinen Komposit-Metall / Holz-Objekts mit Metall-Proben zu simulieren. Um reale Artefakte so gut wie möglich zu reproduzieren, wurden auf natürliche Weise korrodierte Metall-Stücke und blanke metallische Proben parallel getestet. Das Testmetall war Stahl.

Um die Wirkung der Chemikalien zu untersuchen, wurde zuerst eine elektrochemische Methode vewendet. Das Korrosionspotenzial ("$E_{corr}$") wurde im Laufe der Zeit bei den sich in den Lösungen befindenden Proben beobachtet. Die Proben wurden danach zwei komplementären beschleunigten Alterungstesten unterzogen. Der erste Alterungsprozess simuliert das Verhalten des Metalls bei dem Kontakt mit hoch-konzentrierter PEG-Lösung. Dies entspricht dem Post-Imprägnierungszustand eines Composite-Objekts. Dieses Verhalten wurde voltametrisch Punkt für Punkt gemessen . Bei der zweiten Methode setzten wir die Probenstücke zu 30 Nass / Trockenheit- Zyklen in einer Feuchtekammer aus, um unkontrollierte Museumsverhältnisse zu simulieren.

Eins der wichtigen Ergebnisse dieser Untersuchungen ist, dass keiner der hier getesteten Korrosionsinhibitoren, Hostacor IT® miteingeschlossen, bei der Verhinderung von Korrosion in einem späteren 20% (v/v) PEG Imprägnierungsbehandlung effektiv ist. Dies bedeutet, dass ein Eisen / Holz mit Wasser durchtränkten Artefakt, das zur Lagerung in eine korrosionsinhibierende Lösung zuerst getaucht wird, nachträglich nicht die Korrosion der Eisen-Teile in eine "einfache" PEG-Lösung verhindert.

Unter den Korrosionsinhibitoren bei 20% (v / v) PEG-Lösung erschien die Carboxylatationslösung zur Behandlung von Eisen / Holz-Kombinationen aufgrund ihres niedrigen, für die Holz-Komponente schädlichen pH-Werts nicht geeignet.

Die Natrium-decanoate zeigte viel versprechende Ergebnisse bei blankem Stahl, ist aber wie frühere Studien es gezeigt haben, bei korrodiertem Eisen wirkungslos und daher in dieser Situation nicht verwendbar.

Die Natriumnitrit-Lösung zeigte zwar interessante Ergebnisse, aber ihre Kompatibilität mit PEG kann nicht garantiert werden, da sie eine Senkung des pH-Werts der Lösung bewirkt. Ihre Verwendung könnte also die Holzteile beschädigen und den Schutz des Metalls mindern.

Bei allen geführten Experimenten erwies sich Hostacor IT® als der am besten geeignete Korrosionsinhibitor für die Behandlung von Eisen/Holz, von Wasser durchtränkten Artefakten in PEG-Lösung, aufgrund seines neutralen pH-Werts und seiner Fähigkeit korrodierten Stahl zu passivieren. Leider wird diese Chemikalie, die übrigens nicht ganz problemlos ist, demnächst nicht mehr verkauft. Das, abgesehen von anderen Nachteilen von Hostacor IT®, sollte Restaurierungswissenschaftler dazu anregen, weitere Chemikalien außer Hostacor IT® zu entwickeln, die ähnlich wirksam sind.

# 1. Introduction

## *1.1. General introduction to the subject*

*"Conservators are faced with a challenge when they treat objects made from more than one material. This is especially true if the object cannot be taken apart. Treating both materials at the same time can be a problem, since standard treatments for one material may be harmful to another"*[1]. This statement by Selwyn regarding the conservation of waterlogged wood/metal composites is an excellent summary of the issues encountered by conservation professionals with such artifacts[2].

In the early 1980's, Canadian and Australian conservators, confronted by many marine composites, are the first to be concerned by ethical issues often involved in their conservation[3]. Indeed, depending on the artifact and on its conservation state, dismantling the object and treating each component separately might involve damaging or even more destroying one or several other materials[4]. In 1984, the first results of treatment trials in which it was considered that composites should be treated as a whole were published by Cook *et al*.

Since the word "composite" will be widely used throughout this thesis, its definition, within the framework of this study, should be precise. In 1997, in order to enable conservators to ethically justify treatment proposals for composites (dismantling or not?), Mardikian suggested a definition of composites as well as a typology. His definition is the following: *"Assembly, voluntary or not, of two or more materials of similar nature or distinct, that has, during burial in aqueous solution, suffered of physicochemical modifications"*[5]. This definition is thorough in that it concerns all kind of materials and the association of two or more of them. For this study, it was chosen to work on appropriate treatments for non-separable composites made of waterlogged wood and iron. This choice is explained later on. In the following, such objects will be called iron/wood composite artifacts.

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[1] Selwyn, 1993.

[2] North, 1987, p.248; Hawley, 1989, p. 223; Selwyn, 1993; Degrigny, 2004, p.255; Memet and Tran, 2005, p.439.

[3] Cook *et al.*, 1984; North, 1987, p.247; MacLeod *et al.*, 1989; Hawley, 1989; Gilberg *et al.*, 1989.

[4] Mardikian, 1997, p.32.

[5] Ibid., p.33, translated from French.

The next chapter discusses briefly how the study of the conservation of composite metal / wood artifacts in the last thirty years inspired the topic of this thesis: "Testing corrosion inhibitors for the treatment of marine iron/waterlogged wood composite artifacts in polyethylene glycol solution".

## *1.2. Choice of the material for this project*

Polyethylene glycol (PEG) is a chemical commonly used to impregnate waterlogged organics[6]. So far, its use is even considered to be the best wood consolidation treatment[7]. The difficulty with using PEG when a metal is associated with a piece of wood is that it is mildly acidic, and thereby aggressive to metal[8]. In order to fill this gap, two alternatives exist. Either a chemical other than PEG is used to treat the organic part, or a corrosion inhibitor, protecting the metal and compatible with PEG, is added to the PEG during impregnation. Many studies have been performed for both options during the last thirty years[9]. All of them have their advantages and limits[10].

An overview of the research already carried out is needed to show how the materials tested here were chosen. Two major phases can be distinguished in the development of the conservation of iron/wood composite objects. A first period of fifteen years can be called the "general phase". From the beginning of the 1980's (1984) until the end of the 1990's (1998), conservators and conservation scientists studied objects made of different kind of metals connected to different types of organic materials[11]. In the late 1990's, a second period began that can be called the "iron/waterlogged wood phase"[12]. From this moment until now, most of the works have dealt with the treatment of this association of materials.

This focus is not really surprising though since such a combination is particularly problematic for conservators. As iron corrodes very fast, it diffuses quickly in the wood during burial[13]. This often leads to the pieces becoming stuck together (through iron salts) and creates the "non-separable" quality of many marine composites. This problem is less common with composites made of copper alloy and organic: the copper, more noble, corrodes less than iron, and presents bactericidal properties that preserve the organic part[14]. The significant amount of published data available for iron/wood composite

[6] The use of PEG is developed in chapter 3.4.2.

[7] Glastrup, 1997, p.377.

[8] Detailed are given in chapters 3.4.2; 4.2 and 5.3.3.1.

[9] Cook *et al.,* 1985; Hawley *et al.*, 1989; Gilberg *et al.,* 1989; Selwyn *et al.*, 1993; Guilminot, 1998 and 2000; Argyropoulos *et al.*, 1999 and 2000.

[10] Chapter 5.3.3. is a review of these studies.

[11] Cook *et al.,* 1985; Hawley *et al.*, 1989; Montluçon et Lacoudre, 1989; Pennec, 1990; Selwyn *et al.,* 1993; Mardikian, 1997; Guilminot *et al.*, 1998.

[12] Argyropoulos *et al.*, 1999 and 2000; Bobichon *et al.,* 2000; Degrigny et Guilminot, 2000; Guilminot, 2000; Lemoine, 2000; Berger, 2001; Degrigny *et al.,* 2001; Berger, 2003; Memet and Tran, 2004.

[13] Keepax, 1989, p.17; Fisher, 1994, p.13 and chap.4 devoted to iron corrosion and conservation.

[14] North and MacLeod, 1987, p.80; Keepax, 1989, p.18.

objects has oriented this diploma work on these materials in order to compare the results obtained to previous studies.

This "iron/waterlogged wood phase" is also marked by the specific study of the compatibility, efficiency and use of PEG with a particular iron corrosion inhibitor, "Hostacor IT®"[15]. Much research were performed to assess the performance of this corrosion inhibitor in PEG solutions[16]. Also, as this is the most well-known corrosion inhibitor ever studied in association with PEG, its drawbacks are also well documented[17]. As a matter of fact, Hostacor IT® was chosen as the "reference" corrosion inhibitor for this work.

Three « new » corrosion inhibitors were considered within this project. The choice of these chemicals has been guided by recent research on corrosion inhibitors applied to cultural heritage using environmentally friendly compounds[18].

Among this group of new eco-friendly products, the "sodium carboxylate family", studied by French laboratories[19], is of particular interest for the following reasons[20]: they are efficient on several types of metals: Zn, Pb, Cu, Al (non-corroded) and Fe (corroded or not)[21]; easy to prepare; inexpensive; and reversible. Based on the results obtained, two chemicals of this family, the sodium decanoate and the "carboxylatation solution" have been chosen for the present experiments[22].

The last chemical tested here is the sodium nitrite. It has been chosen because promising trials had been performed at The Mariner's Museum® (Newport News, VA, see chapter 1.4) by a corrosion engineering company, CC Technologies, as possible storage solution replacement (with neutral pH) for large artifacts currently soaked in highly alkaline solution (NaOH)[23]. More details about these corrosion inhibitors and the solution tested are given in chapter 7.

## *1.3. Objectives and methodology*

This study has two objectives:

- compare the effectiveness of Hostacor IT®, sodium decanoate, carboxylatation solution and sodium nitrite as corrosion inhibitors in PEG solution;
- assess the "long term" efficiency of these corrosion inhibitors.

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[15] Argyropoulos *et al.*, 1999 and 2000; Bobichon *et al.,* 2000; Degrigny et Guilminot, 2000; Guilminot, 2000; Argyropoulos *et al.* 2000; Memet and Tran, 2007.

[16] *Ibid.*

[17] The drawbacks are discussed in section 5.3.3.

[18] Degrigny *et al.,* 2007; Hammouch *et al.,* 2007; Hollner *et al.,* 2007a and b; Rocca and Mirambet, 2007.

[19] Laboratoire de Recherche des Monuments Historiques and the University of Nancy (France).

[20] Hollner *et al.,* 2007a and b; Rocca and Mirambet, 2007.

[21] Hollner *et al.,* 2007a and b.

[22] *Ibid.*

[23] CC Technologies, INC., 2007, p.57.

The methodology used to assess the effectiveness of the corrosion inhibitors in PEG solution was to simulate the treatment of a non-separable marine composite metal/wood object on metal samples. In order to stay as close as possible to real artifacts conditions, naturally corroded metal coupons were tested in parallel to bare ones. The metal tested was carbon steel. This material is often encountered on modern shipwrecks[24].

In order to compare the performances of the chemicals, the first evaluation method was electrochemical. The "open circuit potential" (also called "rest" or corrosion potential, "$E_{corr}$") has been monitored, over time, on coupons in solution. These $E_{corr}$ measurements provide information about the surface reactivity or stability[25].

The second step, dedicated to the long term effectiveness of the corrosion inhibitors, has been conducted through two different experiments:

- the first one was to simulate the behavior of metal, in contact with high concentrated PEG solution, as it should be after the treatment of a composite object. This has been tested with voltammetric plots[26];

- the second experiment was the reproduction of an uncontrolled museum environment in a humidity chamber followed by optical observations to assess the impact of this accelerated ageing test.

## *1.4. The Mariners' Museum® (Newport News, Virginia)*

In order to perform this project, I had the chance, through a National Oceanic and Atmospheric Administration-funded internship, to be received by the laboratory of the Batten Conservation Complex at the Mariners' Museum® (TMM), Newport News, Virginia, USA. This laboratory has been created to receive and treat parts of one of the icons of the American Civil War, the USS *Monitor*[27].

### 1.4.1. The USS *Monitor*

The ship was designed and built in 1861 over one hundred and forty days. The *Monitor* was very different from other steam warships at the time. Not only was she completely ironclad, but she was smaller, semi-submersible and her main deck feature was a rotating gun turret 20 feet in diameter[28] (fig.1).

[24] Degrigny, Conservation Scientist, written communication, July 2008.

[25] Costa, 2003, p.88; see also chapter 7.

[26] Chapter 7.3 describes the techniques used for this study.

[27] The Mariners' Museum®, USS *Monitor* Center, 2005.

[28] *Ibid.*

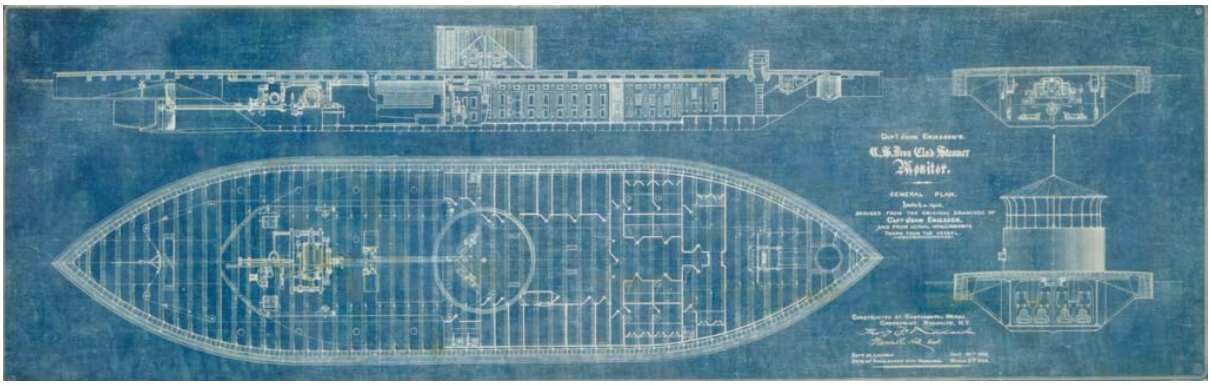

Figure 1: The USS *Monitor* designed by Ericson in 1861. From TMM®.

After fighting a historic battle against the CSS *Virginia*, which ended the era of wooden warships, the *Monitor* sank in a storm off Cap Hatteras, North Carolina, on December 31, 1862. Lost at sea were sixteen of the fifty six sailors on board[29].

The wreck was found in 1973 laid upside down on the seabed, at a depth of 240 feet (73m). In 1975, the USS *Monitor* wreck site was designated the nation's first national marine sanctuary under the management of the National Oceanic and Atmospheric Administration (NOAA). In 1987, NOAA designated TMM® as the repository for all artifacts and archives recovered from the USS *Monitor*. Between 1975 and 2002, excavations from NOAA and the US Navy recovered more than 3000 artifacts including the engine, the propeller and the revolving gun turret[30].

The USS *Monitor* was designed with two 11 inch Dahlgren guns that were located in the rotating gun turret[31]. The conservation of artifacts associated with the guns, such as the bore tools, block and tackle, and carriages includes both metal and organic materials. In many cases these artifacts consist of two or more types of materials[32]. Reflections and studies about appropriate treatments for these artifacts are of real interest for the *Monitor* conservation project.

### 1.4.2. The Batten Conservation Complex at The Mariner's Museum®

The building of Batten Conservation Complex is separated in two main laboratories: the "wet lab" at the first-floor (930m$^2$), and the "clean or dry lab", upstairs (325m$^2$) [33]. They are physically joined. The wet lab is employed for the treatment of large artifacts and for work that might involve wet or dirty operations. This building has been constructed around the tank dedicated to the turret of the *Monitor*[34]

[29] The Mariners' Museum®, USS *Monitor* Center, 2005.

[30] *Ibid.*; Grieve, Conservator at TMM®, oral communication, December 2007.

[31] The Mariners' Museum®, USS *Monitor* Center, 2005.

[32] Nordgren, Senior Conservator at TMM®, written communication, June 2007.

[33] Grieve, written communication, June 2007.

[34] Paden, Artifact Handler at TMM®, oral communication, December 2007.

(4.5m high, 350 000 liter of capacity[35]). The two Dahlgren guns, the gun carriages, the engine of the ship, the condenser, the propeller shaft and two Worthington pumps[36] are currently in different stages of treatment in this room. In order to move these artifacts, a crane, able to carry up to 40 tons, is installed under the roof of the lab. An X-ray room as well as polishing equipment for metallographic samples are also installed in this lab. The clean lab is devoted to smaller artifacts, to analysis equipment (chloride analysis and metallographic microscope) and to the chemical storage area. A ventilation system is installed in this room. Included in the clean lab is a conservation library. Relative humidity and temperatures are controlled in the clean lab, though not in the wet one. Another workroom of 300m$^2$ also includes wet object storage (i.e. a large refrigerator), a photography/digital image processing area, and a freeze-dryer.

For additional analyses the laboratory has collaborations with numerous institutions, such as: the College of William and Mary Materials Characterization Laboratory at Jefferson National Laboratory Applied Research Center (Newport News, VA - SEM/EDS, FT-IR, High-Mag Optical Microscopy), Christopher Newport University (Newport News, VA - Ion Chromatography, analytical chemistry support), Old Dominion University (Norfolk, VA - Mossbauer Spectroscopy, XRD, Potentiostat, Sulfur analysis), University of Minnesota (Studies of *Monitor* wood), University of Calgary (Canada), Stanford University (CA - Wood sulfur content analysis), the Northrop Grumman shipyard (Newport News, VA - Optical Emission Spectroscopy, XRF, FT-IR, High Energy X-radiography, Engineering support), the US Navy (diving, *Monitor* recovery, providing sample material) and hospitals of the area[37].

Eight employees are sharing the significant work involved by the project. They have the following appointments: chief conservator, conservation project manager, senior conservator, conservator, conservation assistant, artifact handler, conservation technician. Another senior conservator, specializing in paintings, is devoted to TMM®'s other collections such as paintings and ship models.

Being part of TMM® laboratory for a ten month internship gave me the opportunity to experiment with cleaning techniques for different materials such as: cleaning of waterlogged wood and leather, deconcretion and cleaning of copper alloys artifacts, and help with deconcretion of large artifacts. The use of chloride analysis apparatus as well as polishing machines was also common.

Several trainings were also dispensed by the laboratory team such as electrochemical techniques, use of the freeze-dryer and the X-ray machine. Other training on high-performance optical microscope and SEM were also followed at the Applied Research Center - College of William and Mary, located at the Jefferson Laboratory (Newport News, VA)[38].

[35] Krop, Conservator Project Manager at TMM®, oral communication, December 2007.

[36] Nordgren, oral communication, November 2007.

[37] Grieve, oral communication, November 2007.

[38] See Jefferson lab, ARC, 2005. The training concerned the high-performance optical microscope, Hirox KH-3000 VD, as well as on the scanning electron microscope, Hitachi S570 SEM.

Lastly, to perform this study, the laboratory was able to purchase all the required equipment while Dr. Desmond C. Cook, from the Physics Department of Old Dominion University (Norfolk, Virginia), also helped significantly by providing access to the research equipment needed for the electrochemical measurements (a potentiostat for voltammetry) and analysis of corrosion products (XRD apparatus).

# *Part I: Study and conservation of non-separable marine iron/wood artifacts: an overview*

Before discussing treatments of composites objects, two chapters will be devoted to the composition, degradation and conservation of waterlogged wood and iron. As introduced before, these two materials were chosen for this work because iron/wood composites have been well studied and are, therefore, a good basis for the type of experiment performed here.

Seawater has been chosen as composite's burial environment since this is the origin of most artifacts conserved at TMM®. Therefore, an overview of seawater properties will be discussed in the following section. Understanding characteristics of the burial environment is a fundamental step in the study of artifact deterioration.

# 2. Introduction to the burial environment: seawater

*"Seawater is a very complex medium composed of pure water, mineral salts, dissolved gases, bacteria, micro- and macro-organisms participating in the food chain, matter in suspension derived from the chemical decomposition of living species, and sediments"*[39] (fig.2).

Seawater can be characterised by: its salinity, its amount of dissolved oxygen, its pH, temperature, depth and microorganisms[40].

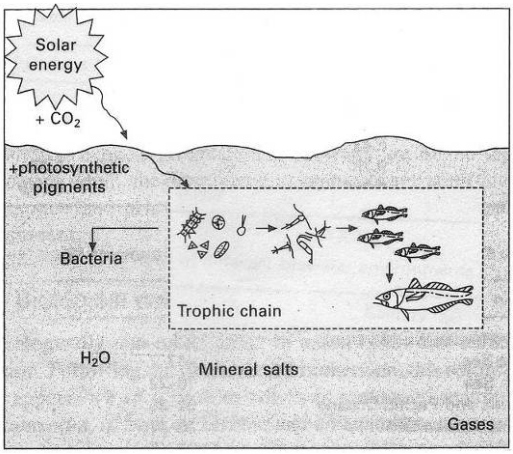


Figure 2: Illustration of the complexity of seawater. From Memet, 2007, p.153.

## *2.1. Salinity*

Salinity is described in terms of conductivity ratio of the fluid[41]. From the conservation point of view, seawater can be considered as a mixture of many dissolved components.

Dissolved salts are present in seawater at 30-40 grams per liter[42] as pairs of ions or complexes[43]. Most are chlorides and sulphates anions, with sodium, magnesium, calcium and potassium for the cations (tab.1).

| Cations (g/L) | | Anions (g/L) | |
|---|---|---|---|
| $Na^+$ | 11.04 | $Cl^-$ | 19.88 |
| $Mg^{2+}$ | 1.30 | $SO_4^{2-}$ | 2.74 |
| $Ca^{2+}$ | 0.42 | $HCO_3^-$ | 0.18 |
| $K^+$ | 0.39 | $Br^-$ | 0.07 |
| $Sr^+$ | 0.008 | $F^-$ | 0.015 |

Table 1: Concentration of the most abundant ions in seawater. From Memet, 2007, p.154 after Roberge, 2000.

This high concentration of chlorides[44] has a significant consequence on buried metal artifacts since it can lead to "active corrosion" with long term damaging effects (see chap.4.3).

The mass of salts in seawater varies from one ocean to another; yet the ratio between each element stays the same. Therefore, the concentration of one component can help to approximate the

[39] Memet, 2007, p.153.

[40] Florian, 1987a.

[41] Memet, 2007, p.153 after Roberge 2000.

[42] Florian, 1987a, p.4; Degrigny, 2004, p.243.

[43] Memet, 2007, p.154.

[44] The chlorides concentration in seawater is almost 20 000 times more than in freshwater (Singley, 1988, p.4).

others[45]. Another important aspect is that the salt concentration increases as the concentration of dissolved oxygen decreases[46]. This means that salinity is higher at the interface between seawater and sediments than it is in seawater[47]. This has a significant impact on the amount of chlorides in the corrosion products of buried artifacts. Additionally, the elevated concentration of dissolved salts in seawater gives it a very low resistivity, making seawater an efficient electrolyte[48]. Electrochemical reactions are therefore highly favoured in this environment. This means that degradation occurs readily for buried metal objects (see chapter 4.3).

## *2.2. Dissolved oxygen*

Oxygen is the most significant dissolved gas that conservators are concerned with, since it is the main "corrosion engine"[49]. The dissolved oxygen concentration varies from one sea to another. But the concentration tends to decrease depending on depth and temperature[50]. However, between 1000 and 3000m depth, dissolved oxygen increases again[51] (fig.3).

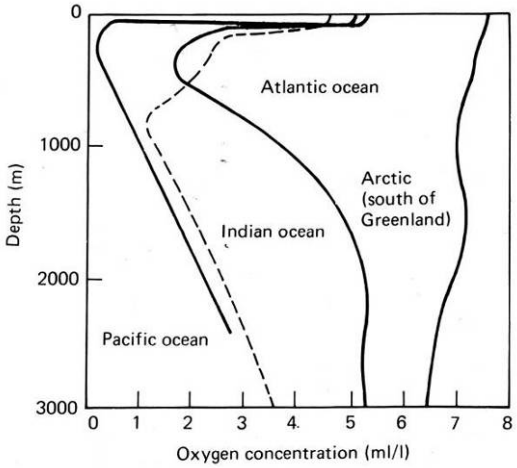


Figure 3: *"Characteristic oxygen profiles of the Atlantic, Pacific and Indian Oceans and of the area of formation of the deep Atlantic waters".* From Florian, 1987, p.5, after Dietrich 1963.

## *2.3. pH, temperature and depth*

With an increase in depth, temperature and pH decrease[52]. The decrease in pH of seawater is limited due to buffering action of $CO_2$ and $CO_3^{2-}$[53]. These compounds maintain the pH between 7.5 and 8.4 (fig.4)[54].

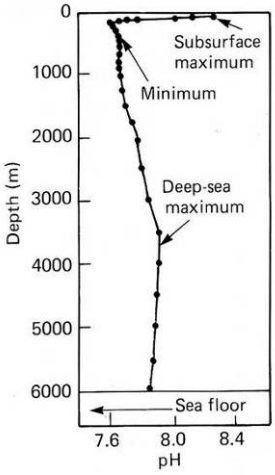


Figure 4: Deep sea pH profile. From Florian, 1987a, p.6, after Park, 1966.

[45] Florian, 1987a, p.4; Memet, 2007, p.154.

[46] Florian, 1987a, p.4; Memet, 2007, p.155.

[47] Memet, 2007, p.154.

[48] North and MacLeod, 1987, p.68; Memet, 2007, p.155. See equation 7, chap.4.2.

[49] Florian, 1987a, p.5.

[50] Florian, 1987a, p.4; Memet, 2007, p.155.

[51] Florian, 1987a, p.4-5; Degrigny, 2004, p.244.

[52] Memet, 2007, p.155.

## *2.4. Biological consideration*

In terms of artifact deterioration, the sulfate-reducing bacteria (SRB) are the most important component of the biota. They metabolize oxygen in anoxic environment by reducing sulfate ions as follows[55]:

$2SO_4^{2-} \rightarrow S + S^{2-} + 4O_2$ Equation 4

Sulphides react then with $H^+$ as follows:

$2H^+ + S^{2-} \rightarrow H_2S$ Equation 5

Chapter 3.3.1 will discuss the possible "active degradation" of timbers due to the formation of hydrogen sulphide following sulfate reduction[56]. The *Vasa*, a remarkable Swedish vessel of the 17th century, is currently suffering from sulfur degradation[57]. Other effects of the SRB on wood and iron will be discussed in the relevant chapters (chap. 3.3.1 and 4.2.2).

Lastly, another significant effect of bio-organisms on metallic artifacts is that they are actively involved in marine concretion formation[58]. This will be discussed in detail in chapter 4.2.2. Also, whenever wood is in contact with metal, e.g. in the case of iron/wood composites, this gangue of concretion tends to cover the whole artifact, not just the metallic compounds[59].

In general, the deeper and more rapidly an object is buried by sediments, the better it is preserved[60]. Indeed shallow waters can favour additional mechanical damage to unburied artefacts due to water movement[61]. This phenomenon is reduced in deep waters and almost non-existent in buried environments[62]. However, specific degradation predictions are very difficult to make and each artifact has to be considered on its own.

To conclude this section, it appears that seawater is an ambivalent environment for artifacts. Low amounts of oxygen, temperature and neutral pH help to preserve objects, but on the other hand, salinity as well as bacteria may be very harmful for them.

[53] Florian, 1987a, p.6. Equations of the dissolution of the carbon dioxide are the following: $CO_{2sol}+H_2O \rightarrow H_2CO_3$ (Equation 1); $H_2CO_3 \rightarrow H^+ + HCO_3^-$ (Equation 2); $HCO_3^- \rightarrow H^+ + CO_3^{2-}$ (Equation 3; Degrigny, 2004, p.244).

[54] Florian, 1987a, p.4.

[55] Florian, 1987a, p.15.

[56] Sandström *et al.*, 2003, p.43.

[57] Sandström *et al.*, 2002a and b; Sandström *et al.*, 2003; Sandström and Fors, 2006.

[58] North and MacLeod, 1987, p.77.

[59] See chapter 5.2.

[60] De La Baume, 1990, p.239; Memet, 2007, p.156.

[61] North and MacLeod, 1987, p.76-77.

[62] Memet, 2007, p.164; Degrigny, written communication, August, 2008.

# 3. Composition, degradation and treatment of waterlogged wood

This section will discuss waterlogged wood conservation as an introduction to composite artifacts. It is essential to understand waterlogged wood composition, degradation and treatment before approaching iron/waterlogged wood composite objects.

## *3.1. Chemical nature of wood tissue*

The main components considered in the following description of wood composition are cellulose, hemicellulose and lignin[63]. Tannins are also mentioned, as additional substances[64].

Cellulose is a polymer made up of glucose monomers in long chain-like particles (i.e. polysaccharide, fig.5g)[65]. The association of about forty cellulose chains forms an elementary fiber. Depending on the links between cellulose chains, the elementary fibers will have a structure either ordered (crystalline[66]), or disordered (amorphous, fig.5e). The aggregation of elementary fibers is called a microfibril[67]. In all environments, the amorphous parts degrade first[68]. The hydroxyl groups of the polysaccharide allow water molecules to be absorbed through hydrogen bonding giving it hygroscopic characteristics[69].

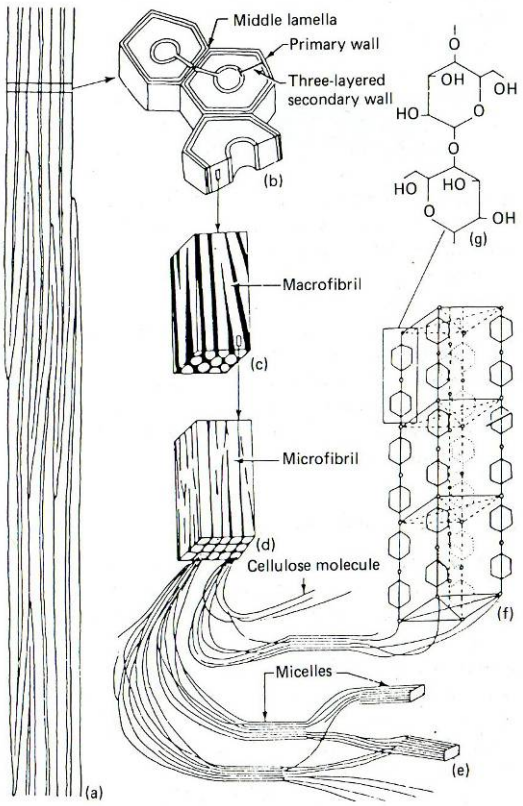


Figure 5: Detailed structure of cellulose. (a) strand of fiber cells; (b) cross-section of fiber cells showing layering; (c) fragment from middle layer of secondary wall showing macrofibrils (white) and interfibrillar spaces (black); (d) fragment of microfibril showing microfibrils (white); (e) structure of microfibrils with crystalline (micelles) and amorphous zones; (f) fragment of micelle showing parts of chain-like cellulose molecules arranged in a space lattice; (g) two glucose residues connected by an oxygen atom – a fragment of cellulose molecule. From Florian, 1987, p.23.

[63] De La Baume, 1990, p.223-224.

[64] Campredon, 2007.

[65] Florian, 1987b, p.25.

[66] These parts are also called micelles (Florian, 1987b, p.23-25).

[67] Florian, 1987b, p.23; De La Baume, 1990, p.224.

[68] Florian, 1987b, p.25; De La Baume, 1990, p.223-224.

[69] Cronyn, 1990, p.239.

Hemicellulose is also a polysaccharide, but is mainly amorphous and presents a lower degree of polymerization than cellulose[70]. There is also a lower proportion of hemicellulose with respect to cellulose in wood structure overall[71]. It is suggested in the literature that hemicellulose acts as *"a hydrated amorphous matrix surrounding cellulose fibrils* [fig.5c]*, preventing aggregation, hydrogen bonding and cocrystallization of the cellulose fibers"*[72].

Lignin and tannins are complex polymers based on phenol[73]. Despite its amorphous structure, lignin is chemically very stable because of its rigid, three-dimensional structure. Lignin is only found in woody plant tissue. Its role is to provide rigidity to the cell walls[74]. Both lignin and tannins act as naturally occurring preservatives in plants[75].

Wood cells structure can be described in term of their growth. The first cell walls that form are called primary walls. They are very thin and thicken gradually by successive deposits of cellulose and hemicellulose layers forming secondary walls[76] (S1, S2 and S3, fig.6). Lignin may be deposited in some primary walls but occur mainly in secondary walls[77]. *"What principally distinguishes each zone of the wall is the differing orientation of the fibrils* [polysaccharide chains] *which spiral around the longitudinal axis of the cell rather like a coil spring"*[78]. The orientation of these chains influences the physical and chemical properties of plant fibres[79]. The compound middle lamella, mostly made of pectic substances, forms the boundary between adjacent cells[80] (fig.6).

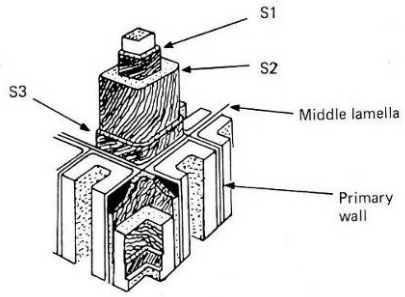


Figure 6: The arrangement of the cell walls in wood showing the orientations of the fibrils in the secondary cell walls, the primary cell walls and the middle lamella. From Grattan, 1987, p.58.

[70] Florian, 1987b, p.28.

[71] De La Baume, 1990, p.223-224.

[72] Florian, 1987b, p.28.

[73] Cronyn, 1990, p.239.

[74] De La Baume, 1991, p.223-224.

[75] Cronyn, 1990, p.240.

[76] Additional compounds such as pectin and protein are also present in very low amount (Florian, 1987b, p.24).

[77] Florian, 1987b, p.24.

[78] Grattan, 1987, p.59.

[79] De La Baume, 1990, p.223-224.

[80] Florian, 1987b, p.28; Grattan, 1987, p.58.

## *3.2. Wood characteristics*

Trees are divided into two groups, hardwood (angiosperms, mostly deciduous trees) and softwood (gymnosperms, conifers)[81]. Both types of trees are similarly composed of cells of different proportions and arrangements depending of their function. The arrangement of the cells in the wood is characteristic of the species.

### 3.2.1. Wood anatomy

For all types of wood most cells are organized with their long axes in the longitudinal direction. Structure of wood consists thereby of interconnecting capillaries, i.e. tubular cells, of various sizes[82]. In softwoods, these capillaries are almost entirely tracheids *"(long narrow tubular cells, blind at both ends and with bordered pits,* [pits are valves which control liquid flow through wood[83]]*). In hardwoods, they are fiber tracheids (fibrous tubular cells of several specialized types giving the wood its strength and with bordered pits)*, *and vessels, that are large diameter pores made up of short wide cells or elements connected to one another by perforations. These conduct water in living tree"*[84]. These tissues, when examined in three different cross-sections (transverse, tangential and radial section) can aid in species identification. The transverse section notably shows the growth rings, which give the age of the trees. These rings are due to the annular seasoning during the growth of a tree[85]. Figure 7 presents the main macroscopic wood features.

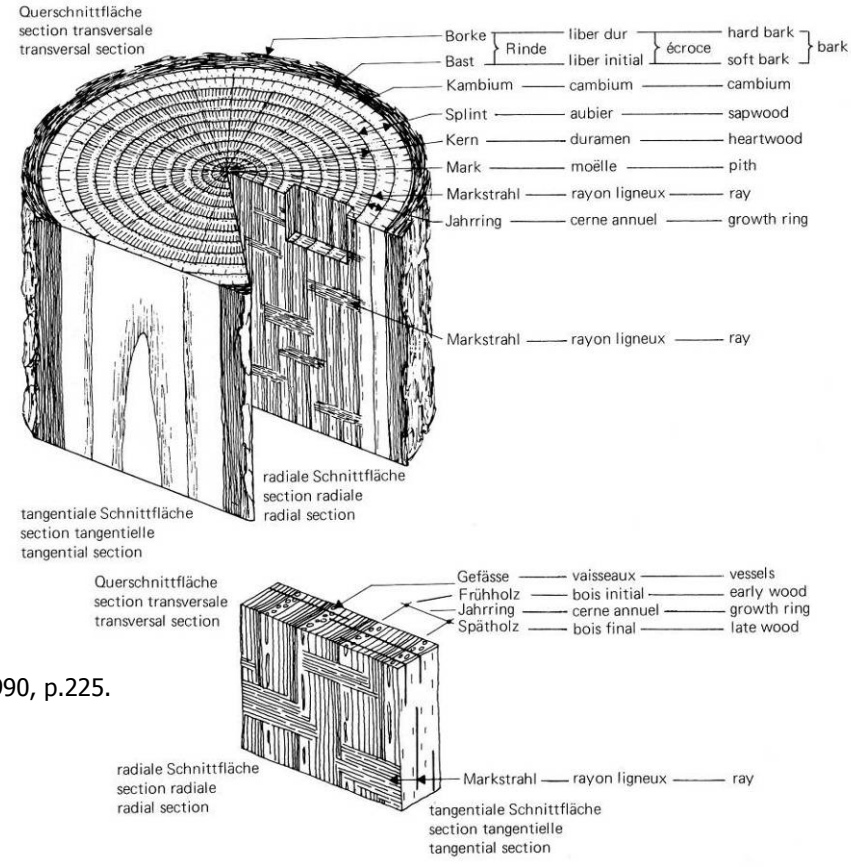


Figure 7: Macroscopic features of wood (exemple of hardwood). From Schweingruber, 1990, p.13.

[81] Cronyn, 1990, p.246; De La Baume, 1990, p.225.

[82] Grattan, 1987, p.56.

[83] *Ibid.*, p.66.

[84] *Ibid.*, p.56-57.

[85] De La Baume, 1990, p.226-227.

### 3.2.2. Water content

The moisture value of wood is called "fiber saturation point" (FSP). When fibers are saturated with water it is referred to as bound water, and water in the empty spaces of the capillary structure is referred as free water. When the wood is dry and reaches a water content below its saturation point, it contracts, shrinks. Inversely, its hygroscopicity makes it swell with a surplus of water[86].

Moisture hysteresis is the difference of humidity between desorption (drying) and adsorption (humidification). After several adsorption and desorption cycles, the hysteresis decreases progressively and the dimensional change of wood is less predictable. During drying, cellulose, hemicellulose and lignin become closer and form links between their hydroxyl groups; water is thus no longer able to be linked to these groups[87].

Wood is also anisotropic, which means that its shape does not change equally in all directions. The ratio of dimensional changes for longitudinal, radial and tangential directions is 1:2:3 (fig.8)[88].

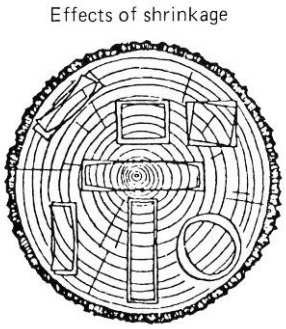


Figure 8: Dimensional behavior of various cuts of wood on air drying. From Grattan, 1987, p.64.

## *3.3. Decay of waterlogged wood*

### 3.3.1. During burial

In general, waterlogged wood can have a good external appearance yet can be very fragile. It can be easily damaged, even by a fingernail or cloth gloves[89]. The degree of decay of a piece of wood will depend on its species. Alder, beech, maple, ash, birch and willow have poor survival in water. On the other hand, oak and yew survive very well[90]. All types of wood are susceptible to important chemical and biological degradations due to water absorption. These two types of decay will be discussed below. In general, physical degradation of wood, underwater, such as breaks, fractures, mechanical failures, is

[86] Grattan, 1987, p.55 and 62; De La Baume, 1990, p.227-228.

[87] De La Baume, 1990, p.227-228.

[88] Grattan, 1987, p.63; De La Baume, 1990, p.227-228.

[89] Cronyn, 1990, p.250.

[90] *Ibid.*

less harmful than chemical and biological ones[91]. Therefore, physical degradation will not be discussed in the following chapters.

#### 3.3.1.1. CHEMICAL DECAY

The major chemical reactions between wood and water are hydrolysis, acid-base transformations and oxidation. Environmental conditions influence their rate[92]. These reactions cause scission of cellulose and hemicellulose chains, especially in the amorphous regions. Scission decreases the polymerisation degree of the molecules and thus weakens them[93]. Additionally, hydrolysis of hemicellulose and cellulose releases a hydroxyl group. These new hydroxyl radicals make the cell walls of the wood to become more hygroscopic[94].

The oxidation reactions are catalyzed by metallic salts contained in water[95]. MacLeod and Richards show that hemicellulose and lignin are hydrolyzed and oxidized faster than cellulose when metallic corrosion products are present[96].

Wood can be stained in two different ways by iron salts. Most frequently, orange/yellow rust stains are observed. When the wood is rich in tannin, black iron tannates are formed[97]. The same metallic salts may also be protective for organics. Iron salts can quickly precipitate from solution on artifacts and can thus "seal" the surface of objects, protecting them from air and humidity[98]. In archaeology, this phenomenon is well documented in necropolis contexts where organics might be preserved in contact with metal in mineralized form[99]. The protective and destructive actions of metallic salts involve compromises when treating waterlogged timbers[100]. This is especially the case for metal/wood composites if a "source" of metallic salts is permanently available near the wood.

Another burial consideration is that extreme acid and alkaline conditions can cause scission of the molecular chains of wood[101]. Florian underlined that hemicelluloses and lignin are more sensitive to alkaline solutions[102]. *"Lignin is sensitive to alkaline degradation, which, due to electrolysis, may occur*

[91] Erosion of the surface of the material is however possible due to currents and suspended particles (De La Baume, 1990, p.234).

[92] De La Baume, 1990, p.237.

[93] *Ibid.*

[94] *Ibid.*, p.241.

[95] *Ibid.*, p.236.

[96] MacLeod and Richards, 1997, p.345.

[97] Degrigny et Guilminot, 2000, p.6.

[98] Keepax, 1989, p.17.

[99] Fisher, 1994. One can also find the term of "pseudomorph" to designate this mineralized preservations.

[100] See chap. 3.3.1.2, 5 and 6.2.1. Also: MacLeod, 1989, p.245.

[101] De La Baume, 1990, p.240.

[102] Florian 1987b, p.27-28.

*on ships where wood is associated with metal"*[103]. Degradation of iron/wood composites, underwater, is discussed in detailed in chapter 5.2.

#### 3.3.1.2. BIOLOGICAL DEGRADATION

Diffusion of water in wood structures results in the invasion of microorganisms. This will readily occur if chemical degradations have already started to weaken the cell network[104].

Damage from boring animals may be present, especially if the piece of wood comes from an aerated marine site or if it has spent time, before burial, in seawater[105]. The shipworm (*Teredo* spp.) and the gribble (*Limnoria lignorum*) are well known for the channels they bore into wood[106]. Beyond that, marine borers and crustaceans as well as ligniferous marine fungi have two major effects: destruction of the cell wall and of the pit membrane[107].

The cellulose chains can be cut by enzymatic hydrolysis catalyzed by certain bacteria[108]. The consequence is that more water and microorganisms can then penetrate the timber[109]. As a result, as the cell wall is attacked, the fiber saturation point (FSP) increases[110]. *"For most woods, this is between 25 and 30% moisture, but it can increase to over 60% for degraded wood. This increase simply represents the increase in internal volume of the cell wall which requires more water to feel it up as degradation proceeds"*[111].

As pits are weakened, permeability of wood becomes considerably enhanced. This phenomenon progresses from the outer surfaces through to the wood core. It creates the characteristically centripetal degradation that is often observed on waterlogged wood[112]. A classification scheme, which groups wood according to the percentage of sound wood versus degraded wood, has been developed by specialists (fig.9)[113]. It is notably based on the moisture content of waterlogged wood. This value is universally used as a degradation indicator. The moisture content is calculated as follow[114]:

$$\frac{(\text{Weight, waterlogged} - \text{Weight, oven dry})}{(\text{Weight, oven dry})} \times 100$$

[103] Florian, 1987b, p.27.

[104] De La Baume, 1990, p.241.

[105] Cronyn, 1990, p.250.

[106] *Ibid.*

[107] Grattan, 1987, p.65.

[108] De La Baume, 1990, p.241.

[109] *Ibid.*

[110] Grattan, 1987, p.65.

[111] *Ibid.*

[112] De La Baume, 1990, p.241; MacLeod and Richards, 1997, p.345.

[113] Grattan, 1987, p.67.

[114] *Ibid.*, p.65-66.

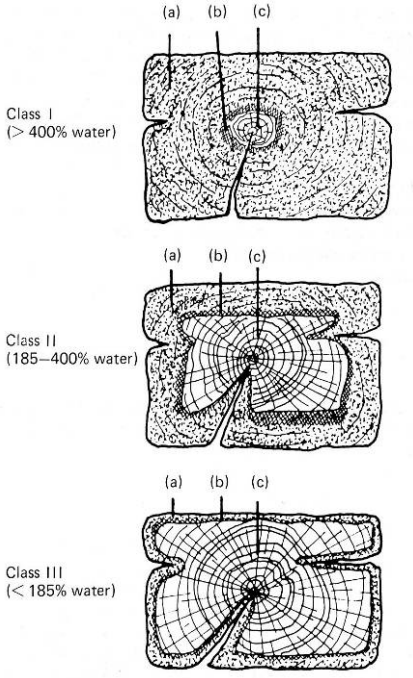


Figure 9: Classification scheme of wood degradation, example of oak. From Grattan, 1987, p.67, after de Jong, 1979.

- (a): very soft and grayish brown layer with very little cellulose;
- (b): thin layer, more fibrous than (a) and has consistency of "old rope";
- (c) has almost as cellulose as fresh oak , is abundant in tannin and seems to be almost impermeable.

Beyond the moisture content, empirically, the three classes can also be defined as follow:
- Class I: has none or very little core in condition (c)
- Class II: has somewhat more (c)
- Class III: has considerable (c)

Unfortunately for artifacts, the largest amount of bacteria is located at the water/sediment interface[115]. Anaerobic bacteria can act up to a depth of 65cm in the sediment[116]. Special attention should be paid to sulfate-reducing organisms (SRB). The effects of these bacteria are a grave concern for wood conservation as well as for composites containing wooden elements. Growth of SRB requires both the absence of dissolved oxygen and the presence of suitable organic material food source such as wood[117]. It has been discussed in chap.2 that SRB's metabolism transforms sulfate ions into sulfides that can form afterwards dissolved hydrogen sulfide (Equations 4 and 5). This compound is a mild acid[118] and therefore acidifies the wood[119].

Beyond that, these organisms are responsible for further consequences. When water rich in $H_2S$ penetrates the wood, other bacteria convert hydrogen sulfide into solid sulfur compounds (e.g. elemental sulfur or other reduced sulfur forms)[120]. Sulfur thereby accumulates in the wood over time. The problem is that, in the presence of oxygen, iron salts, and a relative humidity (RH) higher than 60%, elemental sulfur can be oxidized to sulfuric acid[121]. The metallic salts are catalysts of the

[115] Chap.2 and De La Baume, 1990, p.239.

[116] De La Baume, 1990, p.239.

[117] North and MacLeod, 1987, p.75.

[118] Domjan, 2006.

[119] No reference has been found for this idea, but we will see in chap.4.2.2 that $H_2S$ acidifies the metal (Memet, 2007, p.156). Therefore, it should also affect wood.

[120] Sandström *et al.*, 2003, p.43.

[121] Sandström *et al.*, 2002a, p.55; Sandström *et al.*, 2003, p.43; Fors and Sandström, 2006, p.212-213.

process[122]. This is a post-treatment effect but has to be considered early in the conservation process of an artifact in order to prevent the issue (i.e. remove metallic salts and/or be sure that RH is always under 60% and stable)[123]. Otherwise, the wood becomes acidic and develops fragile, degraded, and spongy/like areas. Sulfate salts precipitating on the surface are visible effects of the acid formation.[124] This problem is currently facing the *Vasa* conservation team in Stockholm but is a general concern for artifacts recovered from the sea[125]. It underlines the dual effects of metallic salts that can preserve and damage the shape of waterlogged wood[126]. It emphasizes too the importance of keeping a stable climate when storing or exhibiting conserved marine-archaeological artifacts. This matter will be revisited again when discussing conservation of iron/wood composites.

Sulfur in its sulfide form appears as a black color on wood[127]. However, as mentioned before (chap.3.3.1.1), this color might also be the appearance of iron tannates. These compounds result of the interaction between wood tannins and iron salts contained in water or iron salts of a metallic object close to the wood[128].

### 3.3.2. Post excavation

*"The fundamental problem is that if waterlogged wood is allowed to dry in an uncontrolled manner, it may collapse, shrink, distort, split, embrittle, check, delaminate and even disintegrate completely. On the other hand, it may suffer from almost none of these effects and yield a perfectly presentable artifact"*[129].

Indeed, a timber removed from its burial environment becomes unstable and is very susceptible to decay. As soon as water begins to evaporate, the cell walls collapse resulting in the object shrinking[130]. When more water is lost, the surface cracks irreversibly.

Another aspect of the post excavation decay is the action of bacteria/fungi. Oxygen exposure provides a substrate for biological species[131]. Bacteria presence can be identified by a soapy/sticky wood surface. Presence of fungi may be recognised by a thin white and grey mycelium layer[132].

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[122] Sandström *et al.*, 2003, p.38.

[123] Sandström *et al.*, 2002a and b; Fors and Sandström, 2006, p.413.

[124] Sandström *et al.*, 2003, p.22 and 58.

[125] Sandström *et al.*, 2002a and b; Sandström *et al.*, 2003; Fors and Sandström, 2006.

[126] Iron salts can thus damage the wood in two ways: by oxidizing cellulose (chap.3.3.1.1) and by being a catalyst of the sulfuric acid formation.

[127] Cronyn, 1990, p.250; De La Baume, 1990, p.239.

[128] Cronyn, 1990, p.250.

[129] Grattan, 1987, p.55.

[130] Cronyn, 1990, p.254.

[131] *Ibid.*

[132] De La Baume, 1990, p.238.

In order to avoid these phenomena, specific precautions and treatments are required. This is the topic of the next chapter.

## *3.4. Treatments of waterlogged wood*

*"The traditional criterion of a 'successful' conservation treatment of wet organic finds has been the extent to which the wet dimensions and appearance have been preserved"*[133]. A good conservation treatment also involve that the artifact reaches an equilibrium with its new environment. This is notably the reason why the removal of metallic salts from such artifacts has to be considered seriously. As it has been mentioned in the previous section, iron salts can act as catalysts of acid formation while they can preserve the wood structure. Also, treatments of waterlogged wood usually involve the further steps: cleaning, consolidation, drying and storage. This chapter is a review of the principal options of these steps, found in the literature.

### 3.4.1. Cleaning

Cleaning waterlogged wood aims to:

- remove sediments leftover from excavation;
- remove staining (mostly iron stain, iron tannates or sulfides) and sometimes exterior material aggregates (concretions) that disfigure the artifact appearance;
- remove iron salts if necessary;
- remove mineral salts of seawater that might crystallize and introduce further tension of the material while drying.

The following treatments proposed should all be performed in aqueous solution to keep the artifact wet until the final consolidation and drying processes. Removal of soil or sediments remains can notably be performed by successive water baths, i.e. intensive washing by baths of water regularly changed[134]. A soft brush can be used during this process if needed[135]. Dental hand tools (ultrasonic or manual) may also be used to remove concretions or metallic stains from the surface of the timbers[136]. If the wood is bound to metal, the concretions might be significant and difficult to remove. A cleaning protocol has been developed at Arc'Antique laboratory (France) for composites, and is discussed in the related section[137] (chapter 5).

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[133] Jenssen, 1987, p.122.

[134] Grattan and Clarke, 1987, p.195.

[135] De La Baume, 1990, p.249.

[136] Grieve, oral communication, November 2007.

[137] Degrigny *et al.*, 2002, p.400-404.

Chemicals can also be employed to clean waterlogged organics, mostly to remove metallic salts[138]. Chelating agents like dibasic ammonium citrate, EDTA (ethylenediamine tetraacetic acid) or ammonium hydroxide may be used. Oxalic, formic or acetic acids, in low concentrations, are also an option for this purpose[139]. The ammonium citrate will be discussed in detail in chapter 5, as it is often considered in literature and practice for the treatment of composite objects[140]. An article of Macleod *et al.* suggests the use of a polyethylene glycol (PEG 800) solution between 5 and 10% (w/v) to remove iron and chlorides from timbers[141]. This last suggestion however starts the consolidation process of the wood, which is not always wanted at this stage of the treatment. "*An interesting point about iron contamination of wood is that chances of removal are much higher if the storage before treatment is kept anaerobic and slightly acidic. This prevents the formation of highly insoluble oxides and hydroxides. These conditions may be obtained by use of very dilute solution of sodium sulphite as an oxygen scavenger*"[142]. Grattan and Clarke also report a treatment of bleaching iron tannates performed by Swiss laboratories in the late 1970's[143]. No information has been found about the effect of this bleaching mixture on the wood structure. In any case, when dealing with chemicals, the pH of the solutions should be checked carefully in order to not treat the wood with excessive acid or alkaline solutions (see chap.3.3.1.1).

Electrophoresis can also be used to remove oxides and metallic sulfides[144]. This method consists of placing the artifact in an electric field, between two electrodes. Good results have been shown in the past, notably on the *Titanic* organic artifacts[145]. It should be avoided on fragile objects as they might be destroyed by the process (unsatisfactory results have occurred on textile fibers[146]).

After cleaning, if the treatment cannot be continued immediately (i.e. still requiring consolidation, drying), objects must be stored properly in water, in chemically stable containers (polyethylene bags or boxes). Fungicide/biocide may eventually be added (Dowicide®, a sodium orthophenyl phenoate, is used when needed at TMM®). Containers should be kept away from oxygen, temperature variations and light. An ideal storage environment is a refrigerator maintained between 2 and 5°C[147].

---

[138] Conservators should be aware that *"among many conservators, the use of anything other than tap water or distilled water is regarded as unacceptable because of the unknown effects of various cleaning agents"*[138] (Grattan and Clarke, 1987, p.194).

[139] Grattan and Clarke, 1987, p.194-195; Grieve, oral communication, November 2007.

[140] Degrigny et Guilminot, 2000, p.7.

[141] MacLeod *et al.,* 1989, p.249.

[142] Grattan and Clarke, 1987, p.195.

[143] Grattan and Clarke, 1987, p.195, after Breaker and Bill 1979.

[144] Montluçon et Lacoudre, 1989; Pennec, 1989, p.132; Berger, 2004, p.23.

[145] Pennec, 1989, p.132.

[146] De La Baume, 1990, p.250.

[147] De La Baume, 1990, p.250. At TMM®, a refrigerator devoted to organics is maintained between these

### 3.4.2. Consolidation

This part of the treatment is fundamental as it aims to physically reinforce waterlogged wood[148]. A consolidation should:

- preserve the artifact's shape and appearance;
- be stable over time;
- be reversible;
- minimally interventive[149].

One of the major challenges of consolidation is to provide a homogeneous treatment when the wood itself is not of homogeneous condition[150]. For example, the core is usually in better condition than the surface (see fig.9, chap.3.3.1). Therefore, before applying a treatment, the condition of the artifact has to be accurately determined in order to select an appropriate solution. The classic "pin test" is a good start to estimate the deterioration of a piece of wood[151].

Once this determination is made, several treatments are possible depending on: the degradation of the artifact, its size, the final storage environment of the object, its final appearance, the cost of the method, its speed, and special hazards or difficulties of the techniques[152].

Several methods will be discussed in this chapter. Polyethylene glycol (PEG) will be considered in detail since it has been chosen as the basis for the tests performed for the current study.

#### 3.4.2.1. POLYETHYLENE GLYCOL

Polyethylene glycol is a linear macromolecule with the general formula $HOCH_2(CH_2OCH)_nCH_2OH$[153]. The "n" determines the length of the chain, and therefore its molecular weight. This number varies from 200 (Low Molecular Weight or LMW) up to 100 000 (High Molecular Weight or HMW). In conservation, the range of PEG used is from 200 to 4000 depending on the wood degradation[154] (see below). These different polymerisation degrees impart different physical properties: LMW PEG is viscous at ambient temperature whereas HMW is solid[155].

temperatures.

[148] De La Baume, 1990, p.253.

[149] Grattan and Clarke, 1987, p.188.

[150] De La Baume, 1990, p.257.

[151] The pin test is an empirical method to assess wood degradation. By simply probing the artifact with a sharp pin, degradation classes I, II or III can be determined (fig.9, chap.3.3.1.2). Grattan, 1987, p.65; Grieve, oral communication, November 2008.

[152] Grattan and Clarke, 1987, p.188.

[153] De La Baume, 1990, p.257.

[154] Grattan and Clarke, 1987, p.169-173; De La Baume, 1990, p.257.

[155] De La Baume, 1990, p.257.

The numerous hydroxyl groups of the molecules make it soluble in water at any concentration. These hydroxyl groups are also able to create strong hydrogen links with cellulose and hemicellulose molecules in wood[156]. Some advantages of PEG include:

- preservation of the shape of artifacts;
- apparent stability;
- theoretic reversibility;
- ease of use;
- excellent penetration into wood structure;
- efficiency of use with large artifacts;
- relatively low cost.

Regardless, significant drawbacks must be mentioned:

- its reversibility is theoretical;
- it is hygroscopic;
- it might be damaged by heat and oxygen;
- it increases significantly the weight of objects;
- the treatment of large objects can be extremely long;
- for n>600, PEG needs to be heated during treatment, to remain soluble in water[157], which can involve expensive apparatus;
- its pH depends on its concentration; commonly used solutions, between 10 to 30%v/v, are corrosive to metal[158].

Even though these drawbacks are important, the advantages presented above leave PEG as the best consolidant for waterlogged wood found in the last thirty years[159].

Like most wood consolidation products (see later in this chapter), the principle of PEG application is that it replaces water in waterlogged wood. It allows water to evaporate while maintaining the shape of the wood. In practice, less deteriorated wood is impregnated with a LMW PEG (usually between 400 and 600) whereas highly deteriorated wood is consolidated with a higher molecular weight (from 1500 to 4000)[160]. The theory is that LMW fits in "small holes" (less deterioration) and HMW in "big holes" (highly damaged zones). However, this simple model must be adapted to the variable conditions of wood. A two step treatment has been developed for artifacts altered in a heterogeneous way in order

[156] De La Baume, 1990, p.257.

[157] Grattan and Clarke, 1987, p.170.

[158] Glastrup, 1997, p.377, 380-381. For metal corrosion in PEG solution, details are given in chap.6.3.1.

[159] Cronyn, 1990, p.258.

[160] De La Baume, 1990, p.257.

to consolidate both the core and the highly degraded external layer[161] (see fig.9, chap.3.3.1.2). To define the proper proportions of consolidiants (LMW and HMW PEG), Cook and Grattan created the software PEGCON that suggests treatments depending on the species considered and their deterioration[162].

As mentioned above, several alternatives to PEG have to be considered depending on the artifact in question. The following paragraphs discuss briefly the most common alternatives.

#### 3.4.2.2. IMPREGNATION WITH RESIN USING A NON-AQUEOUS SOLVENT

- The alcohol-ether treatment

The alcohol-ether method replaces water in the wood with alcohol then introduces a mixture of ether and resin into the wood network[163]. The principle is that the resin adheres exclusively to the cell walls and does not fill the voids in the wood. This allows the timber to remain very light and allows species identification even after treatment. This method is also reversible, which is not generally the case for PEG impregnation[164]. However, this process is very dangerous because ether is flammable at 32°C. Therefore it requires specific and expensive safety infrastructures and should not be applied on large artifacts for safety reasons.

- The acetone-rosin method

An acetone-rosin solution has also been used to impregnate wood. As for the alcohol-ether treatment, the principle is to first remove water from the wood through successive baths of solvent. Then, rosin is added to the solution and impregnates the wooden cells. This method will be discussed again in chap.5.3 since many iron/wood composites have already been treated with rosin[165]. The drawbacks of this method are that it leaves the wood brittle and may not provide a homogeneous impregnation through the whole material[166].

#### 3.4.2.3. SUGAR IMPREGNATION

- Natural sugars

Impregnation with sugar solutions has been used for over one hundred years[167]. Of the several sugars used, the best results were obtained with sucrose (also named saccharose) and sorbitol. However over all, successes of sugar treatments were erratic and the main drawback was the high risk of attack by fungi and microorganisms[168].

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[161] Hoffmann, 1986 and 1990.

[162] Cook and Grattan, 1991.

[163] The final solution is a mix of 70.1% ether, 3.2% dienol, 3.2% castor oil, 16.1% dammar resin, 6.4% rosin and 0.4% PEG (Lang, 2005, after Kramer und Mühlethaler, 1967, p.81-82).

[164] Lang, 2005, after Kramer und Mühlethaler, 1967, p.81-82.

[165] Hawley, 1989, p.237; Guilminot *et al.*, 1998, p.234.

[166] Grattan and Clarke, 1987, p.187.

[167] Grattan and Clarke, 1987, p.181; Hoffmann, 1996.

[168] Grattan and Clarke, 1987, p.181-184.

- Lactilol

Lactilol, a disaccharide synthesized from lactose, can also be a good alternative to PEG. It has antioxidant properties that could make it a good treatment for composite wood/metal objects as it may prevent metal corrosion. The major problem is that it has limited solubility in water which may result in poor impregnation. There are also risks associated with drying artifacts from solution due to lactilol crystallisation within the wood structure[169].

#### 3.4.2.4. *IN SITU* POLYMERIZATION

It is also possible to consolidate wood with polymers that cure after they have fully impregnated the wood. Polymerization can occur through condensation reaction or through radiation catalysis[170].

The principle of condensation reactions implies to mix two components that will react to form a hard resin. Examples are epoxy and melamine-formaldehyde resins[171].

The Arc-Nucléart© method uses gamma radiation to polymerize styrene-polyester molecule added to the wood[172]. The first stage in the Arc-Nucléart© method is to dehydrate the wood through successive solvent baths[173]. The process is advantageous because it has a very short treatment time and it preserves the artifact's shape and appearance well. The Arc-Nucléart method© has already been used on non-separable iron/wood composites[174]. Its drawbacks include: lack of reversibility; impossibility of application to large objects because of the size of the irradiation chamber; use of a costly and hazardous cobalt source to provide radiation. The Arc-Nucléart© laboratory (France) is so far the only one to be equipped to perform this method[175].

### 3.4.3. Drying

Approaches to drying methods depend on the impregnation material. Rosin, resin and *in situ* polymerization treatments use solvents to replace the water in the wood. Artifacts impregnated in aqueous solutions like PEG and sugars are often dried from their water state. Ways to directly dry water from an artifact are discussed below.

The first one, and easiest to perform, is controlled drying[176]. Relative humidity (RH) around the object is slowly decreased in 5% increments. The temperature can be used to regulate the humidity as

[169] Lang, 2005, after Imazu, and Morgos, 1999.

[170] Grattan and Clarke, 1987, p.184.

[171] *Ibid.*

[172] Laboratoire Arc-Nucléart.

[173] *Ibid.*

[174] Hawley, 1989, p.237; Memet and Tran, 2005, p.447.

[175] Laboratoire Arc-Nucléart.

[176] De La Baume, 1990, p.261.

low temperatures decrease evaporation. A humidity buffer such as silicagel can also be used to adjust RH within a closed environment[177].

A second method is freeze-drying. Two types exist: vacuum and atmospheric freeze-drying[178]. The principle of both is to force the sublimation of ice contained in the artifact. The liquid phase is avoided, as are surface tension effects that damage wood tissues. Artifacts have first to be frozen either very fast or very slowly to avoid potential stresses caused by the freezing[179]. Otherwise, objects may need to be treated with a cryoprotector before freezing. PEG appears to have this ability[180]. The major limit of vacuum freeze-drying is that the apparatus is limited in size[181]. Freeze-dryers capable of handling large artifacts are very expensive and therefore not common. The non-vacuum freeze-drying is cheaper and easier to set up. However, treatments can be very long for thick timbers because the water contained in the core of the wood is difficult to sublime without pressure change[182].

Lastly, a new and very promising drying method for waterlogged wood has been developed: it is the use of supercritical fluid. This technique avoids problems associated with the phase changes encountered in other methods[183]. The principle is that, above a certain critical temperature, a fluid can be removed by decompression without any possibility of a liquid phase being formed. As no phase boundaries are crossed, no drying stresses are encountered[184]. The fluid used is carbon dioxide since its supercritical state can be reached at a lower temperature and pressure than water. Prior to this treatment, the treated object has to be dehydrated with methanol because the mixture of water and $CO_2$ could cause important surface tension on the artifact[185]. No addition of resin is required to perform this treatment, which shortens the treatment time (several weeks for methanol/supercritical treatment and several months for PEG and freeze-dried treatment). Researchers are trying to incorporate a resin into the treatment protocol to obtain a stronger final artifact[186]. This method is still being studied and is barely used because its long term success has still not been proven. The current high cost of the

[177] De La Baume, 1990, p.261.

[178] Granttan and Clarke, 1987, p.193-194.

[179] The passage of water from liquid to solid may imply 9% of expended volume (De La Baume, 1990, p.263).

[180] De La Baume, 1990, p.263.

[181] Grattan and Clarke, 1987, p.193-194; De La Baume, 1990, p.262.

[182] Grattan and Clarke, 1987, p.203; Lorin et Lemetayer, 1999, p.118.

[183] Kaye *et al.*, 2000, p.235.

[184] *Ibid.*

[185] Kaye *et al.*, 2000, p.236.

[186] *Ibid.*, p.246.

apparatus is another drawback[187]. This method will also be mentioned in chapter 5.3 since good results have been achieved on iron/wood composites too[188].

### 3.4.4. Storage

A treated artifact should be stored in a stable environment. *"If the material is overdried, it will shrink and distort; if the RH is too high, it will expand; if the RH is fluctuant, the material expands and contracts causing the maximum destruction"*[189]. Above 65% RH, microorganism activity is likely and the recommendation for organics is to maintain a RH between 55 and 60%[190]. A higher RH could also promote sulfuric acid production if sulfur and iron species have not been removed during treatment[191].

[187] Kaye *et al.*, 2000, p.247.

[188] *Ibid.*, p.239-241.

[189] Cronyn, 1990, p.245.

[190] *Ibid.*; Sandström *et al.*, 2002a, p.65.

[191] Fors and Sandström, 2006, p.413.

# 4. Composition, corrosion and treatment of marine iron based artifacts

In order to complete the "materials" discussion, and to better understand iron/wood composite artifacts, an overview of corrosion and conservation of iron based alloys will be discussed in this chapter. A particular emphasis will be placed on carbon steel, as this was the metal chosen for the present experiment. As discussed in the introduction, this modern material is rare in archaeological artifacts but is frequent on modern wrecks (e.g. ships, aicrafts)[192].

## *4.1. Iron structure and general principle of corrosion*

Microscopically, metallic iron can be considered an ordered arrangement (fig.10a) of iron atoms bound together through the positive and negative attractions between electrons and positively charged cations[193]. Unless there is a change in it, the iron metal has a neutral charge.

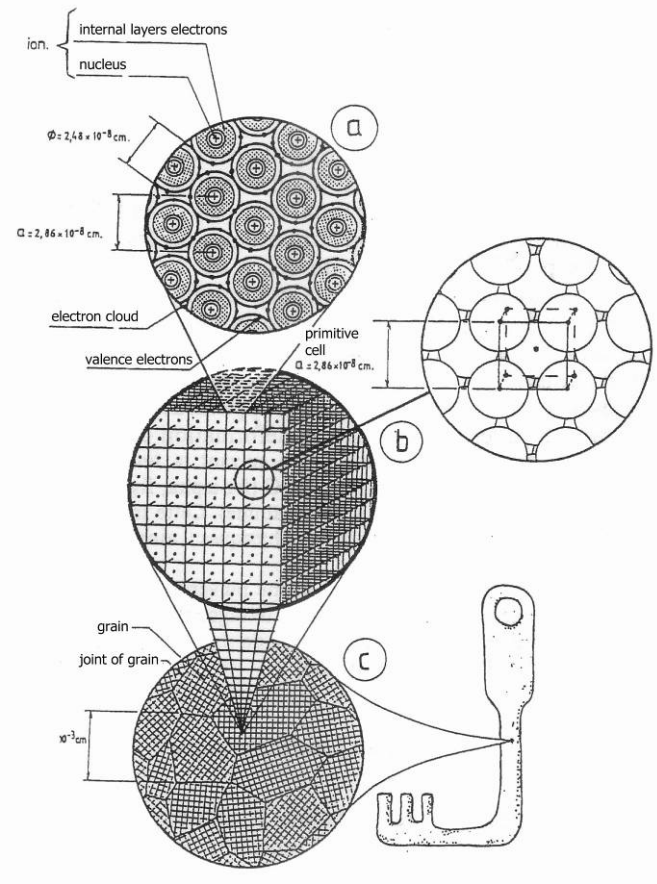


Figure 10: Three representations of iron structure: a) inter-atomic attractions; b) crystalline structure; c) metallographic structure. From Bertholon et Relier, 1990, p.166.

Fundamentally, corrosion is the loss of electrons or cations from this lattice because they are more attracted to the environment than they are to each other[194]. Therefore, as soon as cations or electrons

[192] Degrigny, written communication, July 2008.

[193] Volfovsky, 1999, p.39.

are lost, the cohesion between metallic components is not maintained and the metal becomes unstable (fig.11).

Figure 11: Basic principle of iron corrosion. From Volfovsky, 1999, p.40.

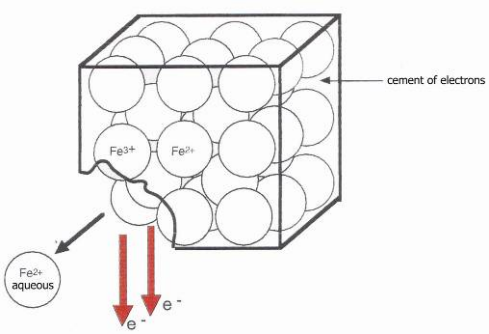


Figure 10b shows the crystalline organisation of iron. Depending on the iron alloying and the treatment received by the piece, this structure can vary[195]. Iron is, for instance, considered a "body-centered cubic" metal[196]. But as soon as it is heated between 910° and 1400°C, it becomes a "face-centered cubic" metal… This crystalline structure will influence metal properties such as plasticity or mechanical resistance[197].

On a larger scale, the arrangement of these crystals is organized in grains, set in different directions (fig.10c). Grain borders are called grain boundaries. These boundaries are heterogeneous and composed of many impurities[198]. These are the sites of intergranular corrosion[199]. The metal also contains inclusions and voids at the micro scale[200]. This description of the metal structure is called metallography. It uses optical microscopy to view the microstructure of a metal[201]. Organization, size and grain orientation depend on the metal or alloy and its manufacturing[202]. The structure might sometimes be complicated, notably when grains have compositional variations, i.e. there are several phases[203].

Metals are also defined by their thermodynamic nobility. The more noble the metal, the less it corrodes. This nobility is expressed in volts and corresponds to an electrochemical potential difference

[194] *Ibid.*

[195] Bertholon et Relier, 1990, p.167.

[196] In a body-centered cubic crystal, atoms are present both at the corners and in the centre of a cube.

[197] Bertholon et Relier, 1990, p.167.

[198] Pernot, 1999, p.65.

[199] Bertholon et Relier, 1990, p. 175.

[200] "Inclusions" are foreign particles ranging in size and composition (Pernot, 1999, p.65). Voids are holes in the metal structures caused by gases as the metal cools (Scott, 1991, p.6).

[201] Pernot, 1999, p.165.

[202] Bertholon et Relier, 1990, p.168.

[203] Pernot, 1999, p.165.

between the metal and its environment[204]. In pure water, for instance, gold has a nobility of +1.500V/$E^0$, copper of +0.337V/ $E^0$, and iron, far from the previous, of -0.440V/ $E^0$ [205]: the higher the potential, the more noble the metal is.

## *4.2. Degradation of submerged iron based artifacts*

When an artifact is submerged in seawater, the most rapid and serious damages are caused by chemical, electrochemical and biological forces[206]. Competitive reactions take place at the surface of the metal due to chemical/electrochemical factors and the adhesion of a biofilm on the artifact[207]. As a result, thick layers of marine concretion are formed around the artifact[208].

Variations of seawater composition affect the environmental conditions (temperature, salinity, pH…) and can produce local physicochemical changes or chemical transformations of the corrosion products[209]. Pourbaix diagrams account for these conditions by considering the effect of pH fluctuations on the electrochemical behavior of metal artifacts. These diagrams show the passivity[210], immunity[211] or corrosion of a metal based on its corrosion potential and the pH of the environment (fig.12). Because they are built from thermodynamic equations this theoretical model can only provide predictions on the electrochemical behavior of metal artifacts in solution (like seawater). Such diagrams can be used too to define preliminary conditions for application of electrochemical treatments (see chap.4.4.1.2; 4.4.2 and 4.4.3).

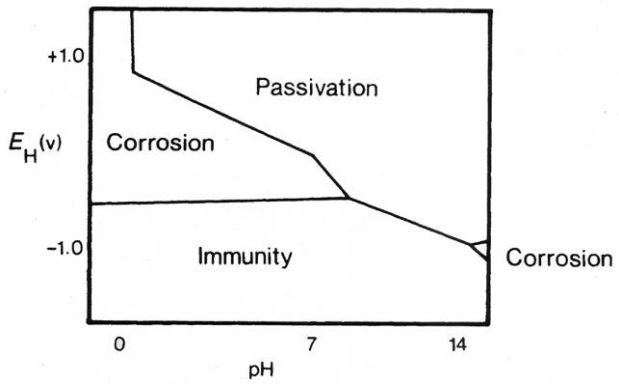


Figure 12: Sketch of Pourbaix diagram for iron in water at 25°C. From Cronyn, 1990, p.188.

[204] Bertholon et Relier, 1990, p.173.

[205] Bertholon et Relier, 1990, p.173.

[206] Degrigny, 2004, p.244; Memet, 2007, p.157.

[207] Memet, 2007, p.157.

[208] North and MacLeod, 1987, p.76; Memet, 2007, p.157. Precisions are given in the following chapters.

[209] Memet, 2007, p.162.

[210] The passivity state of a metal corresponds to a thermodynamic instability. A thin layer of corrosion has been developed at the surface of the metal and acts as a protection against further corrosion (Selwyn, 2004a, p.215).

[211] Immunity is a state of thermodynamic stability. The metal does not react at all with the environment. Metals like platinum and gold are in an immunity state in almost all solutions (Selwyn, 2004a, p.215).

### 4.2.1. Electrochemical reactions involved

In near-neutral aerobic seawater environments, iron corrodes according to the following anodic and cathodic reactions[212]:

$Fe \rightarrow Fe^{2+} + 2e^-$ (anodic reaction) Equation 6

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (cathodic reaction) Equation 7

The overall reaction of these two equations is:

$2Fe + 2H_20 + O_2 \rightarrow 2Fe^{2+} + 4OH^-$ Equation 8

Note that in anaerobic conditions, the cathodic reaction is the following:

$2H^+ + 2e^- \rightarrow H_2$ Equation 9

From a thermodynamic point of view, iron corrosion starts instantaneously in aerobic conditions with the formation of a ferrous hydroxide following the reaction[213]:

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ Equation 10

This ferrous hydroxide is unstable, and its oxidation forms subsequent corrosion products: green rusts (unstable), ferric hydroxides $Fe(OH)_3$ (red/brown color, unstable) and finally ferrous oxy-hydroxides like goethite $\alpha$–FeOOH or lepidocrocite $\gamma$-FeOOH (brown color, stable)[214]. Though stable, these corrosion products are porous and allow diffusion of dissolved oxygen resulting in its reduction on the surface of the metal in the form of $Fe_3O_4$, magnetite (black corrosion product, composed of both $Fe^{2+}$ and $Fe^{3+}$, fig.13), a stable oxide[215]. The rusty-brown exterior layer, composed mainly of oxy-hydroxides, has poor adhesion to the metal whereas the magnetite layer is thick and strongly adhesive to the metal[216]. Recent research has shown that electrochemical reactions start before the formation of a biofilm at the surface of the metal[217].

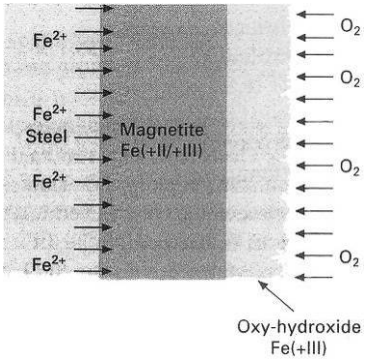


Figure 13: Schematic representation of the early stages of the steel corrosion in seawater. From Memet, 2007, p.158.

[212] Degrigny, 2004, p.245.

[213] Memet, 2007, p.158.

[214] *Ibid.*

[215] *Ibid.*

[216] *Ibid.*, p.159.

[217] *Ibid.*

Obviously artifacts considered within this project had a life before being submerged. Therefore the previous reactions should take into account the presence of an oxide film on the surface of the metal artifacts[218].

### 4.2.2. Biological aspect

#### 4.2.2.1. FORMATION OF THE CONCRETION "GANGUE"

The biofilm formed after few days of immersion is slowly transformed into stable calcite on which new marine microorganisms can attach[219]. As the calcite grows, the corrosion sites change. Anodic sites stay at the metal surface whereas cathodic sites are transported to the surface of the corrosion products. Therefore a new reaction takes place in vicinity of the metal surface[220]:

$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$ Equation 11

Due to $H^+$ formation, the interface between the metal and calcite layers becomes acidic. A higher concentration of ferrous ions is also observed. These ferrous ions migrate to the outer concretion layers where they precipitate[221]. A thick layer of corrosion products and calcite slowly builds around the artifact. One can also find the term of "gangue" of corrosion products[222].

To assure the electroneutrality of the system, negatively charged ions pass from the environment to the metal[223]. These ions are mostly chlorides. Their small size allows them to be very mobile and thus to diffuse easily in dense material. They are widely available in high concentration in seawater[224]. They are especially concentrated at the metal/concretions interface[225]. At this acidic interface, $FeCl_2$ products are formed through oxidation of iron[226].

The formation of corrosion products on iron seems to be rapid during the first several years of burial and decreases slowly over a period of thirty years[227]. This is because the "gangue" of calcite/corrosion acts as a protective barrier[228]. The corrosion rate is remarkably reduced once these concretions are formed[229].

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[218] Degringy, written communication, July 2008.

[219] North and MacLeod, 1987, p.77.

[220] Degrigny, 2004, p.246.

[221] North and MacLeod, 1987, p.77; Degrigny, 2004, p.246.

[222] Memet, 2007, p.157.

[223] North and MacLeod, 1987, p.77; Degrigny, 2004, p.246.

[224] North and MacLeod, 1987, p.77.

[225] Memet, 2007, p.162.

[226] David, 2001, p.34. $FeCl_3$ could be formed too, but as it is stable in highly acidic environment only, it is not as frequent as $FeCl_2$ (same reference).

[227] Memet, 2007, p.159.

[228] Degrigny, 2004, p.246.

[229] Memet, 2007, p.257.

#### 4.2.2.2. FURTHER CORROSION THROUGH MICRORGANISMS

Microorganisms, especially bacteria, engage in further oxidation and acidification of metal. Some reactions involving sulfate-reducing bacteria (SRB) include the following[230]:

| | | |
|---|---|---|
| $4Fe \rightarrow 4\ Fe^{2+} + 8e^-$ | (anodic reaction) | Equation 12 |
| $8H_2O \rightarrow 8H^+ + 8OH^-$ | (water dissociation) | Equation 13 |
| $8H^+ + 8e^- \rightarrow 8H$ | (cathodic reaction) | Equation 14 |
| $SO_4^{2-} + 8H \rightarrow S^{2-} + 4H_2O$ | (bacterial consumption) | Equation 15 |
| $Fe^{2+} + S^{2-} \rightarrow FeS\downarrow$ | (corrosion product) | Equation 16 |

The resulting equation is:

$4Fe + SO_4^{2-} + 4\ H_2O \rightarrow 3Fe(OH)_2\downarrow + FeS\downarrow + 2OH^-$ Equation 17

The iron sulfides that formed give artifacts a black coloration.

The formation of $H_2S$ by SRB mentioned previously can also increase the acidity of affected metals[231] (to a value of 2 at the surface of the metal[232]).

### 4.2.3. Influences of the concentration of carbon on the corrosion of iron based alloys

Although this project focuses on carbon steel, most of the historical and archaeological artifacts are either cast or wrought iron. The following is presenting the specificity of these alloys.

#### 4.2.3.1. CAST IRON

Cast iron is an alloy made of iron, carbon and silicon. The amount of carbon ranges from 2 to 6.7%[233] and silicon from 0.5 to 3%[234]. Depending on the compositions and manufacture particularities, many different carbon/iron phases are formed in the metal[235]. One can notably distinguish grey (e.g. cannon) and white cast iron (e.g. cannon balls)[236]. Grey cast iron usually presents a slightly higher percentage of carbon and silicon than white cast iron. The last is also cooled quickly[237]. This treatment leads to various properties of the two materials (white cast iron is more brittle than the grey one) and to the formation of graphite (made of carbon only) in grey cast iron, while cementite is mainly ($Fe_3C$) formed in white cast iron, in terms of phases[238]. Pearlite, a phase made of cementite elements in ferrite

[230] North and MacLeod, 1987, p.78; Gu *et al.,* 2006, p.924.

[231] The metabolism of SRB involves the formation of $H_2S$ (chap.2, equations 4 and 5).

[232] Memet, 2007, p.156.

[233] Mangin, 2004, p.222. Selwyn, 2004a, p.99 gives a range of carbon from 2 to 4%.

[234] Selwyn, 2004a, p.108.

[235] Degrigny, 2004, p.249.

[236] Selwyn, 2004a, p.108. Degrigny, written communication, August 2008.

[237] Selwyn, 2004a, p.108.

[238] *Ibid.*

($\alpha$Fe) is found in both alloys. As discussed in chapter 4.1, different phases may result in different types of corrosion. Artifacts made of grey cast iron usually have an almost uncorroded metal core surrounded by a layer of graphitized corrosion products[239]. For white cast iron the corrosion spreads deep in the metal core[240]. Graphite forms a three-dimensional interlocking network which preserves the shape of the original object, including surface details[241]. As graphite is a good electrical conductor, it also provides an efficient pathway for electrons from the metal core to the outer artifact surface[242].

#### 4.2.3.2. WROUGHT IRON

Wrought iron contains very little carbon[243]. It consists mostly of low carbon phases such as ferrite with silicate (slag) inclusions from forging. Wrought iron corrosion products are soft and non-adherent, with no retention of original shape and surface details[244]. "*The slag inclusions in wrought iron allow penetration of salt water deep into the bulk of the iron. Subsequent corrosion along the walls of the slag inclusions widens the inclusions and pushes out the slag. As a result crevices are formed in the residual wrought iron which gives it a characteristic wood appearance*"[245].

## 4.3. Deterioration after excavation

When an untreated artifact is exposed to the atmosphere the object can become very unstable[246]. In the presence of oxygen, iron chlorides formed during burial decompose to form new corrosion products[247]. The following electrochemical processes are involved[248]:

$4FeCl_2 + 4H_2O + O_2 \rightarrow 2Fe_2O_3 + 8HCl$ Equation 18

The residual metal corrodes through: $2HCl + Fe \rightarrow FeCl_2 + H_2$ Equation 19

This leads to a cycle that forms and dissolves iron chlorides. This process is called "active corrosion" and the cycle will only stop when no more metal will be found in the artifact[249].

In reality, these reactions are much more complex[250]. They also involve indirect degradations at the surface of the metal, including the growth of acidic drops, cracks, and formation of new corrosion

[239] Memet, 2007, p.162.

[240] Degrigny, written communication, July 2008.

[241] North and MacLeod, 1987, p.79.

[242] Memet, 2007, p.163.

[243] Wrought iron has a carbon content between 0.02 and 2% (Mangin, 2004, p.215).

[244] North and MacLeod, 1987, p.79.

[245] *Ibid.*

[246] Degrigny, 2004, p.251.

[247] Memet, 2007, p.166.

[248] Degrigny, 2004, p.251-252.

[249] Selwyn, 2004a, p.116; Degrigny, 2004, p.252.

[250] Bertholon et Relier, 1990, p.181.

products like akaganéite (βFeOOH)[251]. Akaganéite appears at the surface of an artifact as minute "pipes". The problem of these pipes is that they are built around a chain of chlorides, and are therefore a source of further corrosion[252]…

The issue of active corrosion also affects artifacts recovered from terrestrial sites. However, the urgency of conservation treatment is in line with the severity of chloride content of the metal. Therefore marine artifacts tend to require immediate and intensive attention.

## *4.4. Conservation of marine iron based artifacts*

After the initial documentation of an artifact, the second step is proper storage to ensure that additional corrosion is limited. Further treatment usually includes: cleaning, stabilization (i.e. removal of the chlorides), rinsing, drying and coating for protection[253].

This chapter will briefly review the primary methods currently used by conservators during these phases.

### 4.4.1. Storage prior to treatment

If the artifact is still covered with concretions, they may act as a protective barrier. The artifact can thus be stored temporarily in tap water regularly renewed[254].

As concretions are removed, the newly exposed metal will be very sensitive to the high concentration of oxygen in the environment[255]. Several techniques can be used to prevent or limit any further alteration while in storage[256]:

- immersion in anaerobic conditions (removal of dissolved oxygen).
- passivation in alkaline solution (see fig.12);
- immersion in solutions containing corrosion inhibitors;
- cathodic protection in neutral solutions;

#### 4.4.1.1. DISSOLVED OXYGEN REMOVAL

The corrosion rate of iron can be significantly reduced if dissolved $O_2$ is removed from the storage solution. Several treatments are designed for this purpose: boiling the solution, bubbling an inert gas in the solution (e.g. use of the Soxhlet washing process[257]), and adding an oxygen scavenger (e.g. sodium sulphite which is alkaline)[258].

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[251] Degrigny, 2004, p.152.

[252] Selwyn, 2004a, p.116. For more information about akaganéite, see: Selwyn, 2004b, p.296-297.

[253] Degrigny, 2004, p.257-265.

[254] *Ibid.*, p.259.

[255] Selwyn, 2004b, p.295.

[256] *Ibid.*, p.298-300.

[257] Scott and Seeley, 1987.

[258] Selwyn, 2004b, p.299.

It has also been demonstrated that solutions without oxygen are more effective at removing $Cl^-$ ions than similar solutions with oxygen[259]. However, from that perspective, this method becomes more important for stabilization than for storage.

#### 4.4.1.2. PASSIVATION IN ALKALINE SOLUTION

As seen in chapter 4.2 (Pourbaix diagram, fig.12), passivation of iron can be reached at high pH levels[260]. Therefore alkaline baths of NaOH (0,5M or 2%w/w) or KOH are commonly used as storage solutions[261]. High concentration of chlorides in the solution might compromise though the passivation effect[262].

Sodium carbonate ($Na_2CO_3$) can also be an alternative[263] because it is less hazardous than sodium hydroxide[264]. Compared to sodium hydroxide, a very high concentration of $Na_2CO_3$ is needed though in order to reach the appropriate pH. It is also less soluble than sodium hydroxide[265]. $Na_2CO_3$ might also lead to the formation of insoluble carbonates when used with hard tap water[266]… Sodium sesquicarbonate is another alternative mentioned by Hamilton[267].

In order to follow the behavior of an artifact in such solutions, its corrosion potential ($E_{corr}$) can be monitored over time[268]. Passivation of a bare metal in alkaline solutions is observed through an increase in corrosion potential values. This investigative method is simple and can be highly helpful in determining whether the metal is actually passivating. It requires only a reference electrode, a multimeter and connecting wires[269]. If the artifact is still partially covered with corrosion products, the corrosion potential will decrease first, and increase afterwards (fig.14). This corresponds to the time necessary for the solution to reach the remaining metal surface[270].

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[259] Selwyn, 2004b, p.299.

[260] Which is not a good point for potential related organics… See chapter 3.3.1.

[261] Degrigny, 2004, p.259.

[262] Selwyn, 2004b, p.299.

[263] North, 1987, p.225.

[264] Nordgren, oral communication, 05/08.

[265] North, 1987, p.225.

[266] *Ibid.*

[267] Hamilton, 1999, File 9.

[268] Degrigny, 2004, p.260; Degrigny and Spiteri, 2004, p.330.

[269] Degrigny, 2004, p.260.

[270] *Ibid.*

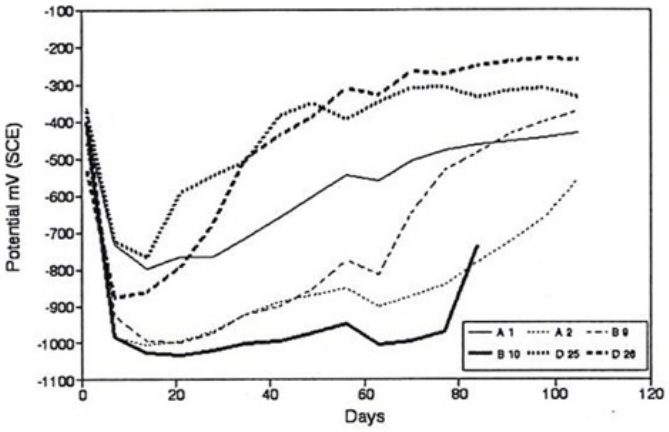


Figure 14: Ecorr/time of archaeological iron in NaOH at 0.5M. From Degrigny, 2004, p.261, after Hjelm-Hansen, 1991.

In some cases the $E_{corr}$ variations are not so descriptive. In this situation, either a high amount of chlorides is affecting the passivating action of hydroxide ions; or the corrosion products are so thick that the alkaline solution cannot reach the metal to provide passivation[271]. The monitoring of both chlorides and $E_{corr}$ is a good way to better understand the processes that are happening around the metal in such solutions[272].

#### 4.4.1.3. CORROSION INHIBITORS

Although L. Selwyn discusses the possibility of using corrosion inhibitors in her recent article about iron degradation and conservation[273], this method is not often commented upon in articles about marine iron based artifacts.

The principle of a corrosion inhibitor is to slow either the cathodic reaction (i.e. oxygen reduction) or the anodic reaction (i.e. iron corrosion) at the surface of the metal[274]. For that purpose, an anodic inhibitor must reach the metal of an artifact whereas a cathodic inhibitor must reach the corroding iron (e.g. graphitized corrosion layer on grey cast iron or conducting corrosion products such as magnetite)[275]. The limitation of such chemicals is that they usually have been developed for use in industry on new metal and their long term effects are unknown. Additionally industrial practices do not necessarily account for inhibition through corrosion layers[276].

Sodium nitrite or carboxylate based inhibitors, like Hostacor IT® or a solution of carboxylatation are examples of iron corrosion inhibitors. These inhibitors are the focus of this research, and their properties and application in the conservation field will be discussed in chapter 7.

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[271] Degrigny, 2004, p.261.

[272] *Ibid.*

[273] Selwyn, 2004b, p.299.

[274] *Ibid.*

[275] Ibid., p.300.

[276] *Ibid.*

#### 4.4.1.4. CATHODIC PROTECTION

The artifact must have a substantial core of metal left for electrochemical techniques to be applied[277]. Cathodic protection with sacrificial anodes and using an impressed current are the two electrochemical methods employed to protect, during storage, a marine metal artifact[278].

Cathodic protection is a very promising method, notably for composite iron/wood artifacts, as it can be utilized in neutral solution like tap water. As mentioned before, treatment in a harsh chemical can cause serious damage to organics[279].

The conservation lab at The Mariners' Museum® uses cathodic protection in its "impressed current" system for three large artifacts: the two gun carriages of the USS *Monitor* and her turret[280]. The gun carriages are extremely complicated objects due to their size, number of components and composite materials. They will be described in chapter 6.6.

The principle of the impressed current is to introduce a low amp direct current into a circuit made of an artifact (cathode) surrounded by anodes, made of stainless metal, both immersed in tap water[281]. The electrons provided to the artifact favor the reduction of the oxygen dissolved in the solution and offer then a good protection to the object (see chapter 4.2.1). To determine the potential to apply to the artifact or the current of the circuit, the use of a potentiostat is required[282].

Another way to promote cathodic protection on an artifact is to connect it to a less noble piece of metal (zinc, aluminum or magnesium alloys)[283]. The less noble metal will corrode first, thereby protecting the artifact. The dimensions of the sacrificial anode must be calculated not to offer an overprotection to the artifact[284].

### 4.4.2. Removing concretions

The $Cl^-$ ions will diffuse into a treatment solution more readily if the porosity of the corrosion layer can be increased[285]. Therefore, it is advantageous to remove concretions before treating marine metal artifacts[286]. Cleaning an artifact should be preceded by radiography (X-ray). Important features can be

[277] Previous x-ray if there is doubt (Selwyn, 2004b, p.299).

[278] Selwyn, 2004b, p.299.

[279] See chapter 3.3.1.

[280] Nordgren *et al.*, 2007, p.55.

[281] Nordgren, oral communication, May 2008.

[282] A potentiostat is an apparatus used to plot voltammetric curves (Degrigny, 2007a).

[283] Shreir *et al.*, 2003, chap.10.2.

[284] Degrigny, writen communication, July 2008.

[285] Selwyn, 2004b, p.298.

[286] North, 1987, p.223; Degrigny, 2004, p.261.

revealed (surface details, exact shape, location of different parts, small finds integrated in the gangue of larger ones…) and fragility estimated based on the interpretation of the images[287].

Mechanical cleaning and electrochemical cleaning are two methods commonly used to remove concretions in conservation laboratories and they are often used together[288]. Another cleaning method, less frequently employed due to cost issues is the hydrogen plasma[289]. This latter technique will not be described in the following since it has never been used on marine metal artefacts still wet.

#### 4.4.2.1. MECHANICAL CLEANING

Mechanical cleaning is particularly suited to hard and compact concretions. Once again, the gangue should be carefully examined before breaking it. *"Mineralized metal, waterlogged wood, ceramics and glass can easily be damaged during the process"*[290]. A variety of tools can then be used to remove concretions. A common method is with a hammer, striking at right angles to the surface of the underlying objet[291]. Attention should be paid to always keep concretions between the object and the hammer[292]. Picks or chisels of different sizes might also be adapted to the cleaning, depending on the artifact. The concretion, and thereby the object, should also be kept wet during the process to avoid any drying problems[293]. Protective clothing (lab coat, gloves, glasses) are required as deconcretion is *"a very messy and possibly hazardous job, with bits of broken concretion flying everywhere"*[294]. Once the concretions have been broken, further cleaning can be carried out with vibrotools, compressed air-driven pens, dental tools and probes, etc[295]. Greatest care should be paid when working on grey cast iron since the graphitized corrosion layer is very soft and can be readily damaged[296]. Also, the cleaning of artifacts such as cannons requires to remove concretions from inside the barrel. This can notably be done with a hydraulic drill and the original cannon bore must be measured carefully before drilling[297].

#### 4.4.2.2. ELECTROCHEMICAL CLEANING

Electrochemical cleaning is well adapted to porous concretions[298]. It requires an electricity-conducting solution, called electrolyte, a tank resistant to this solution[299], two electrodes, including the

[287] North, 1987, p.210; Cronyn, 1990, p.190; Hamilton, 1999, File 9.

[288] Nordgren, oral communication, May 2008.

[289] Schmidt-Ott and Boissonnas, 2002.

[290] Pearson, 1987, p.108.

[291] North, 1987, p.210.

[292] Pearson, 1987, p.108.

[293] *Ibid.*

[294] Ibid., p.109.

[295] North, 1987, p.208-212; Pearson, 1987, p.109; Hamilton, 1999, File 9; Degrigny, 2004, p.261.

[296] North, 1987, p.210.

[297] *Ibid.*

[298] Degrigny, 2004, p.261.

artifact, and an external direct current supply (DC)[300]. The artifact to clean is made the cathode and is connected to the negative terminal of the DC. Positively charged metallic ions travel to the cathode when an electric current is passed through the system. Reduction reactions occur at the cathode and hydrogen is evolved[301]. The anode, connected to the positive terminal of the DC, usually consists of a stainless steel mesh surrounding the artifact[302] (fig.15). Electrons and negatively charged ions travel to the anode when current is applied and oxidation reactions occur at that electrode[303]. *"The two electrolytes commonly used in conservation for treatment of iron objects are alkaline solutions of sodium carbonate ($Na_2CO_3$) and sodium hydroxide (NaOH)"*[304]. In such conditions, this method cannot be used on composite artifacts containing waterlogged wood because of the high pH of the solution.

The principle of the method is to apply an electric potential to the artifact in order to artificially provoke the water reduction into hydrogen. This leads to the formation of hydrogen bubbles at the artifact-concretion interface which can push concretions from the object[305]. The current to apply depends on the composition of the artifact[306].

A good contact between the cathodic electric cable and the residual metal of the artifact should be insured. A small portion of the artifact is usually well cleaned in this purpose[307]. For grey cast iron, the contact has to be made through the graphitized corrosion layer. In this case, small holes can be drilled and a stainless steel rod is gently driven into it for good contact[308].

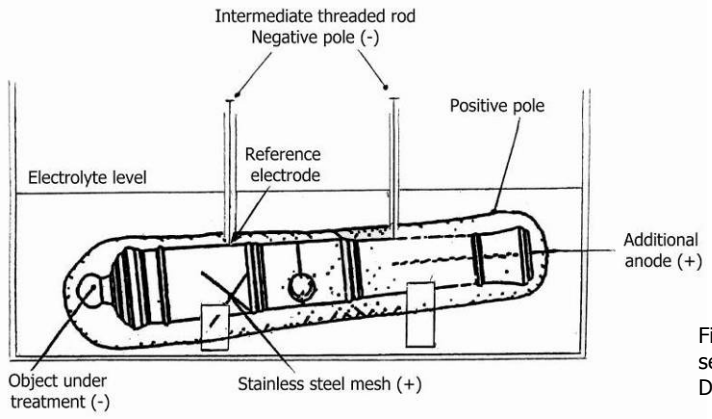


Figure 15: Sketch of the electrolytic deconcretion set up for a grey cast iron canon. From Lacoudre et Degrigny, 1999, p.121.

[299] Details about container construction can be found in: North, 1987, p.224-225; Hamilton, 1999, File 10A.

[300] Hamilton, 1999, File 10A.

[301] Hamilton, 1999, File 10A.

[302] *Ibid.*

[303] *Ibid.*

[304] Hamilton, 1999, File 10B. See also North, 1987, p.225.

[305] Lacoudre et Degrigny, 1999, p.120; Degrigny, 2004, p.262.

[306] North, 1987, p.225.

[307] *Ibid.*, p.224.

[308] *Ibid.*

This method is powerful and has to be carefully used, particularly to avoid excessive hydrogen bubbling that could damage the artifact, or when other objects might be trapped in the concreted layers[309]. Electro-chemical deconcretion is not recommended on wrought iron because its original surface will be lost[310]. On the other hand, grey cast iron can be reliably treated with this method because the graphite layer is an excellent electro-conductor and there is little damage of the original surface[311].

### 4.4.3. Stabilization

As mentioned previously, the principle of stabilizing marine metal artifacts is to remove the bound chlorides from the material in order to prevent active corrosion[312]. Electrolysis (cathodic polarization) is a very common stabilization method used in conservation laboratories[313]. Other treatments like simple washing, alkaline sulfite, high temperature annealing or subcritical water are also mentioned in literature. These last techniques present technical or ethical issues that will be underlined later in this chapter.

#### 4.4.3.1. ELECTROLYSIS (CATHODIC POLARIZATION)

The electrolysis treatment set up is similar to that used for electrochemical deconcretion[314] (fig.15). As for the previous method, specially outfitted tanks must be used to withstand the harsh alkaline environment[315]. The artifact is also made cathode, i.e. polarized cathodically (-) and the stainless steel mesh encircling the artifact is polarized anodically (+)[316]. For the stabilization step the current values are such that the cathodic potential of the artifact under treatment is just above the potential corresponding to the actual hydrogen formation measured with a potentiostat[317]. At the cathode, the corrosion products are reduced during this process, hence the term "Electrolytic Reduction" (ER). For example $Fe^{3+}$ is reduced in $Fe^{2+}$ notably resulting in the decomposition of akaganeite releasing trapped chlorides. This reduction of corrosion layers allows chlorides to more readily diffuse out of the artifact (porosity of the corrosion products is increased) [318]. Practical details on how to apply current to artifacts

[309] Hamilton, 1999, File 9.

[310] Degrigny, 2004, p.263.

[311] Lacoudre et Degrigny, 1999, p.120.

[312] North, 1987, p.213.

[313] North, 1987, p.221-227; Degrigny, 2004, p.264.

[314] Lacoudre et Degrigny, 1999, p.124.

[315] North, 1987, p.224-225; Hamilton, 1999, File 10A.

[316] Selwyn, 2004b, p.301.

[317] Degrigny, written communication, August 2008.

[318] Lacoudre et Degrigny, 1999, p.121.

can be found in publications[319]. They should however be determined, prior to treatment, with a potentiostat[320].

While the stabilization is in progress, chloride extraction is monitored by regularly measuring the chloride content of the NaOH solution[321]. Plots of chloride concentration versus time (or square root of time) are useful for determining end points of treatments[322]. The NaOH solution is replaced when graphs show a plateau or when the chloride content has reached 2000ppm[323] (such concentrations provokes stainless steel's pitting[324]). The treatment is stopped when the $Cl^-$ ion concentration in the solution stays low, usually 20ppm[325] (at The Mariners' Museum® lab, conservators proceed to extraction till values as low as 1 to 10ppm).

#### 4.4.3.2. OTHER OPTIONS

- Washing method

The washing method mentioned above consists of simply soaking the artifact in an alkaline solution[326]. The amount of chlorides removed from the artifact and in the solution is monitored in the same manner as for electrolysis stabilization. This technique, however, is rarely used nowadays due to the unreliable results obtained[327]. Practical details about it are given in the literature[328].

- Alkaline-sulfite

The alkaline-sulfite method takes advantage of reducing corrosion products, using sodium sulfite, to increase the porosity of corrosion layers (same idea as ER). This results in more efficient diffusion of the chlorides from the artifact[329]. For grey cast iron this method is beneficial because it tends to harden the soft graphitized corrosion layer[330]. Treatment baths must be sealed from the environment. Indeed, oxygen in the air rapidly reacts with $SO_3^{2-}$ oxidizing it into $SO_4^{2-}$, thereby destroying the alkaline sulfite reductive capacity[331]. This issue makes this method difficult to afford for laboratories specialized in large underwater artifacts since the cost of sealed containers for cannons can be substantial.

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[319] North, 1987, p.225; Hamilton, 1999, File 10A and B.

[320] Degrigny, 2007a.

[321] Selwyn, 2004b, p.298.

[322] North, 1987, p.223.

[323] *Ibid.*

[324] Degrigny, written communication, August 2008.

[325] Selwyn, 2004b, p.298.

[326] North, 1987, p.221.

[327] *Ibid.*

[328] North, 1987, p.221-222.

[329] North, 1987, p.222; Selwyn, 2004b, p.301.

[330] North, 1987, p.223.

[331] *Ibid.*, p.222.

- Hydrogen reduction/Annealing

Another stabilization method mentioned in the literature is the annealing method. The artifact can be heated in an oxidizing atmosphere or in a reducing hydrogen atmosphere[332]. In both cases, the metal must be heated to a 1000°C in order to volatize the chlorides trapped in the metal[333]. Although initial results appeared effective at removing chlorides, the temperature fundamentally changes the metallographic structure of the metal[334]. The annealing method is no longer advised for ethical issues[335].

- The use of subcritical water

Recent studies are working to transform akaganeite into stable corrosion products through the use of subcritical water. Initial results are highly promising though more work is required to predict the reliability of the method[336].

### 4.4.4. Final conservation steps

#### 4.4.4.1. RINSING

Following any conservation treatment (electrochemical, chemical or mechanical), it is necessary to remove insoluble oxide sludge, metallic powder, residual chlorides and chemical residue through extensive rinsing[337]. Successive baths of de-ionized water are used to ensure thorough rinsing. When the artifact was previously immersed in alkaline solution, the pH of these baths is regularly checked in order to monitor properly the rinsing process. If the rinsing is not complete, remaining sodium hydroxide may lead to the efflorescence of white $NaHCO_3$ crystals, which may cause cracks in materials such as graphitized grey cast iron, or damage wrought iron[338]. However, prolonged de-ionized water baths may corrode the metal. The addition of glucose based acids has been proposed to the rinsing water to prevent this phenomenon[339]. A cathodic protection system can also be set up especially when dealing with grey cast iron artifacts[340]. This is also a good way to protect the metal during the last rinsing steps, when the pH is too low[341]. Hamilton also suggests boiled water as a rinsing treatment which leads to a "pleasing black color" [342].

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[332] Hamilton, 1999, File 10B.

[333] North, 1987, p.227 and Hamilton, 1999, File 10B, after Arrhenius *et al.*, 1973.

[334] North, 1987, p.227; Hamilton, 1999, File 10B.

[335] Hamilton, 1999, File 10B.

[336] De Vivies *et al.,* 2007, p.30.

[337] Hamilton, 1999, File 10B; Degrigny, 2004, p.265.

[338] North, 1987, p.222.

[339] Hamilton, 1999, File 10B.

[340] Degrigny, 2004, p.265.

[341] Degrigny, written communication, July, 2008.

[342] Hamilton, 1999, File 10B.

The rinsing process might take several months[343].

#### 4.4.4.2. DRYING AND FINAL CLEANING

Artifact drying can be accomplished through the addition of heat, vacuum desiccation or dehydration in water-miscible alcohol or acetone[344]. This last method is probably the safest for the artifact[345]. Simple air drying is also used in laboratories. It avoids any stress due to heat, vacuum, or safety issues involved with solvents (particularly for large artifacts)[346]. Stains and undesirable features can be removed by mechanical cleaning (brushing, air abrasion…)[347].

#### 4.4.4.3. COATING

A treated artifact should be protected from the effects of environmental variations (relative humidity and temperature, chemically active vapors or gases). The coating should be impervious to water vapors and gases, natural looking, reversible and transparent in order to easily detect any sign of corrosion[348]. A common treatment is an acrylic layer followed by a microcrystalline wax layer[349]. The two layers assure a durable coating[350]. Other solutions and materials can be found in the literature[351].

#### 4.4.4.4. STORAGE AND DISPLAY

In England, recent research about archaeological iron display suggests that *"an environment of 15% RH or lower would be required, with RHs below 30% retarding the corrosion rate to a low level[852]"*. This study concerns artifacts that are contaminated with chlorides. However, even after having performed carefully the necessary steps of desalination, the remaining chlorides in the core of an object are difficult to detect. Therefore, for any archaeological material, especially for sea-recovered ones, the relative humidity level suggested by Thickett and Luxford, for display, which is also good for storage, should be considered. The previous data are based on the fact that akaganeite formation has been reported at 19% RH. *"A second threshold at 30% when deterioration increase dramatically was also observed"[853]*. Thickett and Luxford improved, with manufacturers, the performances of cases in order to maintain such RH with silica gel over one year. This passive method seems to be a good media

[343] North, 1987, p.222.

[344] Hamilton, 1999, File 10B.

[345] North, 1987, p.229-231; Hamilton, 1999, 10B.

[346] Degrigny, written communication, July 2008.

[347] Degrigny, 2004, p.265.

[348] Hamilton, 1999, File 10B.

[349] Degrigny, 2004, p.265.

[350] Boissonnas, 2005.

[351] North, 1987, p.229-231; Hamilton, 1999, File 10B.

[352] Thickett and Luxford, 2007, p.105.

[353] *Ibid.*

to keep low RH[354]. With less adapted cases than the ones developed by the English Heritage, the storage or display RH levels should be checked regularly. For the storage of treated artifacts, the fundamental rule is to keep a stable environment[355].

[354] *Ibid.*, p.108.

[355] Boissonnas, 2005.

# 5. Application to non-separable marine iron / wood composite artifacts

As mentioned in the introduction, the major issue encountered by conservators dealing with composite artifacts is to decide whether or not the artifact should be dismantled and each component treated separately. Indeed, considering that *"generally, the methods available for treating one component of the artefact will cause the deterioration of the other component and vice versa"*[356]. The dilemma of acidic PEG corroding metallic compounds, at the concentrations commonly used in conservation, was introduced above[357]. This problem is discussed in section 5.3. In the early 1980's the conservation community began pursuing methods that would treat a composite artifact as a whole[358]. Also, prior to a discussion regarding composite degradation and conservation, the definition of composite artifacts should be reviewed.

## *5.1. Composites definition and typology*

As mentioned in chapter 1.2, in 1997, Mardikian suggested a definition and a typology of composites to enable conservators to propose ethically safe treatments for these objects (taking them apart or not?)[359]. His definition has been given before and is mentioned again below: *"Assembly, intentional or not, of two or more materials of similar or distinct nature, that has, during burial in aqueous solution, suffered of physicochemical modifications"*[360]. Mardikian distinguished five classes of composites[361]. They are discussed below accompanied of examples (notably from the USS *Monitor*).

- Type 1: the different parts of the artifacts have been originally assembled with reversible procedures and the object can still be dismantled.

This first type corresponds to artifacts assembled with bolts, keys, or pins, which can still being removed, treated, and reused to reassemble the artifact after treatment[362]. A saxophone from which the keys have been removed before treatment can illustrate this type of composite[363]. A complication

[356] North, 1987, p.247.

[357] See Chapters 1.2 and 3.4.2.

[358] Cook *et al.*, 1984; North, 1987, p.247; MacLeod *et al.*, 1989; Hawley, 1989; Gilberg *et al.*, 1989.

[359] Mardikian, 1997.

[360] *Ibid.*, p.33, translated from French.

[361] *Ibid.*, p.35-36.

[362] *Ibid.*, p.35.

[363] Degrigny, 2007b.

for this type of artifacts appears if an organic part changes dimension during treatment and thereby cannot be reassembled exactly[364].

- Type 2: the different parts of the artifacts have been originally assembled with reversible procedures but the burial conditions were such that the artifact cannot be dismantled without damaging one or several materials[365].

Examples of this type recovered from the USS *Monitor* are notably the Worthington pumps (fig.15)[366]. They are complex composites made of grey cast iron, wrought iron, copper alloy, lead-based sealing compounds as well as gaskets and valve seals made of natural rubber[367]. They were designed to be completely dissembled but although conservators tried to remove as many parts as possible during treatment, some parts were corroded together galvanically, causing fragile graphitized cast-iron components and preventing complete dismantling[368].

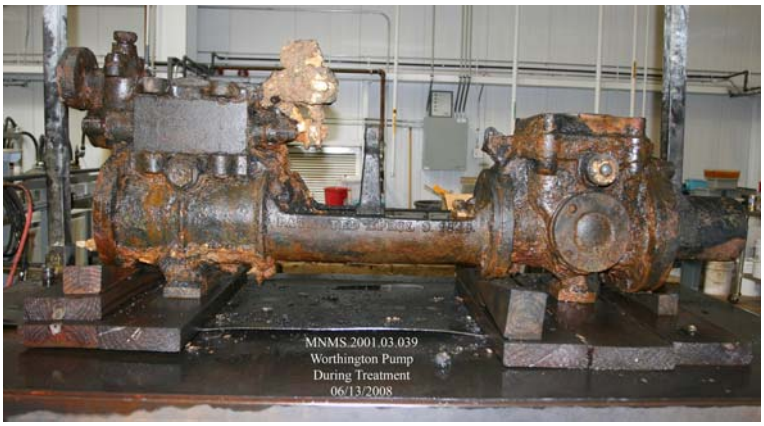


Figure 15: Starboard Worthington pump of the USS *Monitor*. From TMM®.

- Type 3: originally the different parts were assembled with irreversible procedures. Separation of the parts involves the destruction of one material or the modification of the assembling procedures.

Examples of this type are numerous. They vary from knives made of a metallic blade and an organic handle to fire arms with metal and wood. A thermometer recovered from the USS *Monitor* is made of copper alloy, with both ends made of wood surrounded by metal.

- Type 4: several objects or materials have been stuck together by chance during burial.

This is notably the case of artifacts stuck in the concretion gangue of another object (glass, ceramic, tools…). Another common example is coins stuck together through corrosion products.

- Type 5: the artifact presents characteristics of several types.

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[364] Mardikian, 1997, p.35.

[365] North, 1987, p.247; Mardikian, 1997, p.35; Berger, 2004b, p.22.

[366] The Worthington pumps were used for pumping feed water to the boilers, pumping out the bilges (bottom areas) of the ship, fire fighting and other general pumping tasks (Nordgren, written communication, August 2008).

[367] Nordgren, written communication, August 2008.

[368] *Ibid.*

This can be the case of large artifacts recovered from shipwrecks such as the engine from the USS *Monitor*. These artifacts, on their own, are complex composites. In addition, smaller, nearby objects can easily become concreted to the larger artifact.

This fifth type can also include:

- artifacts that were not intended to be dismantled but can be after burial. An example of composite cannon balls is given by Degrigny[369].

- artifacts that were originally composites but are no longer. Galvanic corrosion between metals of different nobility might lead to the complete oxidation of one material with respect to the other[370].

Mardikian's typology is convenient for conservator to describe composite artifacts. However, a classification of composites can also be made based on materials depending on the need of the conservators, archaeologists or curators.

Composites considered within the framework of this diploma, iron/(waterlogged) wood artifacts, can include examples of all types considered by Mardikian. However, the first type is rare due to specific degradations of iron and wood underwater which often lead to the pieces being bound together. The degradation of iron/wood composites underwater is the topic of the following chapter.

## 5.2. Specific degradation of marine iron/wood composite artifacts

As with all objects and materials, the degradation of metal/wood composite artifacts is initiated during their life. This phenomenon is emphasized when the artifact is buried underwater. Besides the specific degradations of iron and wood, further mechanisms arise from the interactions of these two materials[371].

At the iron/wood interface, privation of oxygen and degradation of both wood and iron generate the formation of cations ($H^+$ and $Fe^{2+}$) at the anodic site. In parallel, at the surface of the artifact, iron corrodes in aerobic conditions releasing anions ($OH^-$, cathodic site, see also Equation 8). Conductive properties of metal allow then bonds between these sites and ions to circulate. As shown in figure 16, one of the consequences of this phenomenon is that chlorides will be readily attracted at the iron/wood interface.

Another direct consequence is that the iron/wood interface decreases in pH due to an increased amount of $H^+$ (Equation 11). These conditions favour further iron corrosion and dissolution. Iron salts are therefore ready to interact with wood component. As mentioned in chap.3.3.1.1, iron salts catalyze

[369] Degrigny, 2007b.

[370] North and MacLeod, 1987, p.86.

[371] Translated from: Degrigny et Guilminot, 2000, p.6.

the decomposition of polysaccharides[372]. The depolymerization of polysaccharides such as cellulose and hemicellulose is caused by the release of hydroxyls through the following reactions[373]:

$$Fe^{2+} + O_2 \rightarrow Fe^{2+}OO^{\bullet} \quad \text{Equation 20}$$

$$Fe^{2+}OO^{\bullet} + RH \rightarrow R^{\bullet} + HOO^{\bullet} + Fe^{3+} \quad \text{Equation 21}$$

$$H_2O + HOO^{\bullet} \rightarrow H_2O_2 + OH^{\bullet} \quad \text{Equation 22}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \quad \text{Equation 23}$$

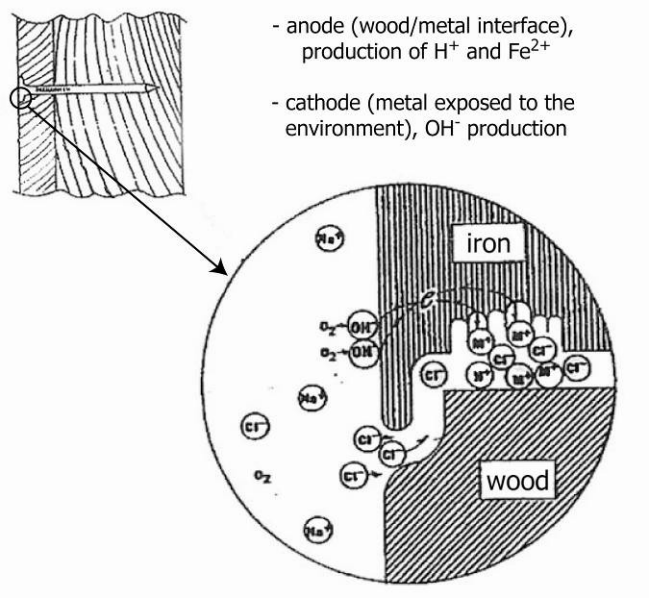


Figure 16: Confinement zone in composites. From Degrigny et Guilminot, 2000, p.6 after Baker, 1980.

The iron ions in solution diffuse into the wood structure and precipitate onto the cellular material. Through this phenomenon, the wood is strengthened[374] and a strong bond between the two components can be formed[375]. In this case, as mentioned in chapter 2, the whole artifact can also be surrounded by the concretion gangue formed by iron during burial.

Iron degradation is also influenced by the humidity levels at the wood metal boundary (during use and immersion)[376]. Iron diffusion into wood can appear as orange/yellow rust stains or the black iron tannate products[377].

Also, removing iron salts from wood which is heavily impregnated with them can cause damage due to the loss of imparted strength. The possible bond formed between the two components (due to iron

[372] De La Baume, 1990, p.236.

[373] Degrigny et Guilminot, 2000, p.6.

[374] Degrigny et Guilminot, 2000, p.6. See also chap.3.3.1.1.

[375] Hawley, 1987, p.224; Berger, 2004, p.22.

[376] Degrigny et Guilminot, 2000, p.6.

[377] *Ibid.* Also mention in chap.3.3.1.1.

salts) forms the basis of the argument against separating wood-iron composite artifacts as discussed in chap.1: either the wood or the metal can be damaged. But on the other hand, remaining salts have hygroscopic properties that can make the artifact reactive to moisture. As mentioned in previous chapters, iron salts, in an object affected by SRB, can act as catalysts for sulphuric acid production such as the *Vasa*'s problem[378].

This issue leads into the other effects of SRB on composites. During burial, the bacteria produce $H_2S$ that acidifies both wood and iron, increasing their deterioration[379]. Also, as underlined by Degrigny and Guilminot, "*The absence of oxygen in the metal/wood interface limits the biodegradation of wood but favors the action of sulfate-reducing bacteria, which is able to consume more iron*"[380]. The formation of FeS through the SRB metabolism has been seen in chap.4.2.2.2 (Equations 12 to 17).

In summary:

- anodic and cathodic sites formed at the interface iron/wood favor the attraction of chlorides at this interface;
- iron and wood are damaged by the increase of acidity at their interface due to both localised $H^+$ formation at anodic sites (role of wood on iron during use and immersion) and formation of $H_2S$ by the SRB;
- wood is both damaged and preserved by metallic salts (role of iron on wood);
- iron corrosion is increased by the high humidity level of the interface;
- a post-treatment relative humidity over 60% can activate sulfuric acid generation which can damaged both wood and iron where SRB was active.

Lastly, the following factors influence the degradation of these composites: the nature of their burial environment, the duration of their burial, the type of wood, the type of iron, and the presence of dissimilar metals[381]. Three condition categories can be made: a good general state; a partial degradation of both parts (metal oxidized, surface of the wood damaged and impregnated with metallic salts); significant degradation of both parts (metal totally mineralized, core of the wood damaged and full of metallic salts)[382].

[378] See chap.3.3.1.2.

[379] See chap.3.3.1.2 and 4.2.2.2.

[380] Degrigny et Guilminot, 2000, p.6.

[381] *Ibid.*

[382] *Ibid.*

## *5.3. Current treatments for non-separable marine iron/wood composites artifacts*

The treatment objectives for marine iron and waterlogged wood remain the same even when the two materials are combined in a composite artifact. However achieving these objectives requires combining methods in order to treat the composite as a whole. Often, since the wood is considered as the most fragile component, the treatment protocol is focused on treating the organic part as best as possible while insuring the stability of the metal. This chapter discusses the different stages of treatments proposed in the literature.

### 5.3.1. Storage of iron/wood composites before treatment

An artifact may need to be stored during its documentation or before/during its treatment. The following options for inseparable composites are commonly used:

- reburial;
- storage in water;
- storage in water under impressed current;
- storage in sodium carbonate solution;
- storage in an aqueous solution with a corrosion inhibitor;
- storage in a solution containing ammonium citrate, PEG 400 and a corrosion inhibitor at neutral pH.

The next paragraphs discuss these possibilities.

#### 5.3.1.1. REBURIAL

Reburying the artifact is an interesting possibility since the object is not stressed with a new environment. The amount of dissolved oxygen changes though around the artifact[383]. However, with the addition of some monitoring equipment, the corrosion potential of the metallic component can be checked regularly and the artifact treated promptly if any deterioration is noted[384]. The RAAR (Reburial and analyses of archaeological remains) project currently carried out in Marstrand, Sweden, should provide interesting results on the behavior of historic metals and wooden elements reburied[385]. However the issue of the composites is not addressed.

#### 5.3.1.2. STORAGE IN WATER

The simplest way to store artifacts is to place them in containers with water and protect them from light and fluctuating temperatures[386]. A refrigerator kept between 2 and 5°C is a favorable environment

[383] Nordgren, oral communication, July 2008.

[384] Degrigny, 2004, p.257.

[385] Bergstrand and Nyström, 2007.

[386] Degrigny et Guilminot, 2000, p.7.

for storing composites in hermetically sealed polyethylene boxes. This protection against light and heat prevents microorganism's development.

Reverse osmosis water (RO) appears to be better at preventing microbiological growth than tap water[387]. However, because of the high cost of producing RO water, laboratories cannot usually afford it in large volumes. Deionized water is more common but is also used in moderation to reduce costs. Hamilton offers the following advice for iron storage solutions that can also be applied to composites: *"Most conservation literature recommends that all storage solutions be prepared with distilled or de-ionized water. The exception to this rule occurs when the material to be conserved contains more chloride than is present in the local water supply. Tap water should be used for all storage solutions and electrolytes until the chloride level of the solution is less than that of the tap water"* [388].

Additionally, removing dissolved oxygen from water through nitrogen bubbling is also a good way to assure a more protective environment for the artifact[389]. This protection system is rarely used due to its prohibitive cost.

The major drawback noticed by conservators while storing composites in water is the development of microorganisms. This was notably the case during the storage of concreted iron/wood rifles at the Arc'Antique laboratory (Nantes, France). To prevent this, conservators changed regularly the water and cleaned the artifact and the tanks with alcohol[390].

Another issue is the corrosion of the metal component that normally occurs in neutral solutions (see fig.12, chap.4.2).

#### 5.3.1.3. STORAGE IN WATER UNDER IMPRESSED CURRENT

As mentioned in chap.4.4.1.2, this technique is currently used at TMM® for the storage of large composites, such as the gun carriages and the turret[391]. In contrast to simple storage in water, this method allows conservators to regularly monitor the condition of the metal without exposing the organic compounds to harmful chemicals or environments. Conservators at TTM® have noticed that, using this technique, pH decreases over time[392]. Also, problems of biological growth might occur due to the humid environment. Lastly, a significant drawback of this method is that it is dependant on a reliable electrical supply (i.e. hurricane or thunderstorms can be an issue for the electrical system)[393].

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[387] Memet and Tran, 2005, p.448.

[388] Hamilton, 1999, File 9.

[389] Hawley, 1989, p.231; Degrigny et Guilminot, 2000, p.7. Dissolved argon seems to work well too (Nordgren, oral communication, July 2008).

[390] Degrigny *et al*. 2002, p.400.

[391] Nordgren *et al*., 2007, p.59.

[392] Secord, Conservator at TMM®, oral communication, August 2008.

[393] Nordgren, written communication, August 2008.

#### 5.3.1.4. STORAGE IN SODIUM CARBONATE

A solution of 2%(w/v) sodium carbonate in tap water or deionized water is proposed in the literature[394]. However there seems to be a knowledge gap relating to the effect of sodium carbonate on organic components. The pH of the solution, around 10, should be aggressive for organic compounds.

#### 5.3.1.5. STORAGE IN CORROSION INHIBITORS

The addition of a corrosion inhibitor to the storage solution is advised by several specialists[395]. Benzotriazole is cited by Hawley for the storage of both copper and iron/wood based composites[396]. 1-2%(v/v) Hostacor IT® in water is used at Arc'Antique laboratory (Nantes, France)[397]. Two issues were noticed by conservation professionals: the efficiency of Hostacor IT® decreases with time and a significant amount of microorganism growth occurs after a few weeks of immersion (even if the artifact was previously soaked in alcohol to prevent microorganism's growth)[398]. Further research was performed to optimize the treatment. Early results showed that storage solutions should be changed as soon as the chloride amount of the solution is higher than 900ppm[399]. The issue is that an "adsorption competition" occurs at the surface of the metal, between the chloride and the inhibitor. This leads to a decreased efficiency of Hostacor IT®[400]. From a biological aspect, the compatibility of several biocides in the solution has been tested. It appears as if sodium orthophenyl phenoate, Dowicide®, is effective and compatible with Hostacor IT®[401].

The effect of Hostacor IT® and benzotriazole on wood has not been studied yet[402]. Therefore, even if these chemicals have already been used on composites, their impact on wood should be examined to avoid short and long term degradation of organic components.

#### 5.3.1.6. STORAGE IN AMMONIUM CITRATE AND PEG 400 AT NEUTRAL PH

MacLeod *et al.* proposed soaking the object in a combined aqueous solution of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 at neutral pH. It *"appears to be a suitable storage medium for wood-iron composite artefacts"*[403]. An appropriate corrosion inhibitor should be added to minimize corrosion of the metal in this solution. MacLeod *et al.* recommended oxalate or tannate[404]. The

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[394] Hawley, 1989, p.226.

[395] Hawley, 1989, p.236 ; Lemoine, 2000, p.41; Degrigny *et al.*, 2002, p.404.

[396] Hawley, 1989, p.236.

[397] Lemoine, 2000, p.41; Degrigny *et al.*, 2002, p.404. The composition of Hostacor IT® is developed in chap.5.3.3.3.

[398] Memet and Tran, 2005, p.450-454.

[399] *Ibid.*, p.452.

[400] Guilminot, 2000, p.157.

[401] Memet and Tran, 2005, p.453.

[402] Guilminot *et al.*, 1998, p.241; Lemoine, 2000, p.41; Degrigny, oral communication, December 2007.

[403] MacLeod *et al.,* 1994, p.208.

[404] *Ibid.*, p.204.

interesting aspect of this suggestion is that ammonium citrate at neutral pH has been tested on wood though oxalate and tannate have not. A surface of iron-impregnated oak was examined and showed no adsorption of the citrate[405]. Also, according to Hawley, wood is more resistant at ambient temperature to immersion in ammonium citrate (2% v/v) than in deionized water alone[406].

In addition, this storage treatment starts the consolidation process of iron/waterlogged wood objects. Ammonium citrate is a powerful chelating agent that removes metal salts from wood while PEG begins to impregnate it. PEG also appears to have chelating affinity on the $FeCl_2$ and other iron corrosion products[407]. To sum up, this storage solution seems very promising but conservators must be aware that it also imparts some consolidation to the artifact.

#### 5.3.1.7. Review

Conservators should remain aware of the following drawbacks of the proposed storage solutions:

- a reburial process is difficult to monitor depending on the location of the laboratory and the site. It also involves a change of the environment of the artifact that has to be considered;
- oxygenated water itself is corrosive to metal;
- a decrease of pH might occur with the impressed current system; bioorganisms growth is not prevented; and this method requires a reliable current supply;
- the effect of sodium carbonate on wood is not known and the relatively high pH of the solution is not adapted to organics;
- the effect of corrosion inhibitors on wood still has to be tested;
- the mixture of ammonium citrate, PEG and a corrosion inhibitor starts the impregnation treatment which is not always wanted. Also, the action of corrosion inhibitors on wood fibers still needs to be assessed.

It should also be mentioned that the corrosion potential of the artifact can be monitored while stored in any of the above solutions. This simple method can indicate whether the iron is stable or is actively corroding. This allows for immediate intervention should a problem arise.

### 5.3.2. First treatment steps: documentation, concretion and salts removal

#### 5.3.2.1. Documentation

The complexity of composites requires thorough documentation before any conservation intervention. X-ray radiography is especially useful on determining how the metal/wood components are joined. X-radiography can show the deterioration of the metal parts and to which extent the wood has been mineralized by iron. A superficial cleaning to remove shells and pebbles incrusted in the

[405] MacLeod *et al.,* 1994, p.199.

[406] Hawley, 1989, p.232.

[407] MacLeod *et al.,* 1994, p.202.

concretions is sometimes suggested for better resolution of the X-rays[408]. This technique is essential to clean the artifact properly[409].

#### 5.3.2.2. CONCRETION REMOVAL

Just as for marine iron and wood artifacts, concretions should be removed from a composite artifact. It will reveal the original surfaces and allow free access for the aggressive species to diffuse from both the wood and the iron components[410].

For composites, mechanical cleaning is more appropriate than electrochemical methods since the alkaline electrolytes could damage the wood (see chapter 4.4.2). A description of the removal of concretions from marine rifles has been published by French conservation professionals[411]. Their idea was to cut the concretion mass in small fragments for controlled removal. Alternating use of an electric cutter, drill and chisel allowed them to carry out the deconcretion step without damaging the soft surface of the wooden components. Figure 17 illustrates their procedure[412].

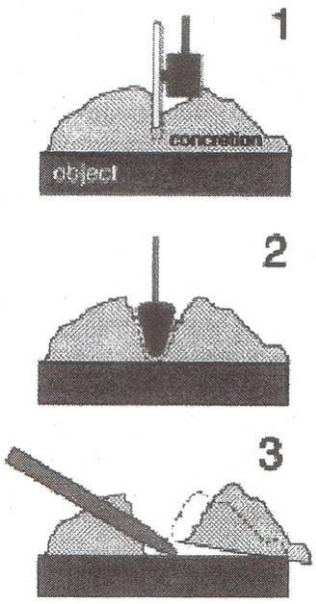


Figure 17: Three steps of the concretions' removal proposed. From Degrigny *et al.*, 2002, p. 401.

Memet and Tran mention that this part of the work took between thirty and fifty hours for one rifle. Due to the long treatment time, they recommended a judiciously chosen storage solution to avoid further degradation of the remaining components during the deconcretion process[413]. Some of the rifles were placed in 1%(v/v) Hostacor IT® in RO water. The authors noticed the formation of "stalactite shaped" corrosion products (fig.18). Their analysis found that the products were highly chlorinated oxides and hydroxides. These stalactites were noticed only at the interface wood/metal showing that this interface was highly active and could not prevent the corrosion of the metal part.

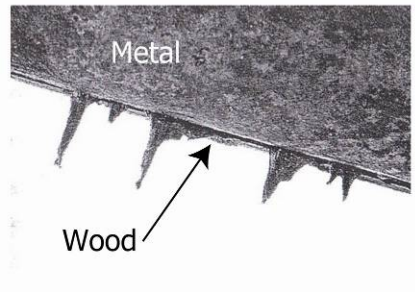


Figure 18: Corrosion products in stalactites shape found at the interface iron-wood of rifles stored in 1%(v/v) Hostacor IT®. From Memet and Tran, 2005, p.443.

[408] Degrigny *et al.*, 2002, p.400.

[409] Mardikian, 1996, p.163 ; Degrigny *et al.*, 2002, p.400.

[410] Degrigny *et al.*, 2002; Berger, 2004a, p.98; Berger, 2004b, p.22.

[411] Degrigny *et al.*, 2002, p.400-404.

[412] *Ibid.*, p.404.

[413] Memet and Tran, 2005, p. 444.

#### 5.3.2.3. REMOVAL OF THE METALLIC SALTS FROM WOOD

As mentioned previously, metallic salts have a double action on wood; they provide structure reinforcement and also catalyze wood degradation. Removal of metallic salts should only be considered after evaluation of the extent of decay[414]. The decision depends on the general condition of the mineralized wood (determined from X-ray) and of the future storage environment. As discussed before[415], if the relative humidity around the artifact rises above 60%, sulfuric acid can be formed from iron sulfate. Once this occurs, the degradation of the organic component can be irreversible[416]. If the artifact can support the removal of the metallic salts, the advised treatments are outlined below:

- the use of chelating agent solutions like EDTA salts (ethylenediamine tetraacetic acid) or ammonium citrate[417];

- a mixture of sodium dithionite at 5% w/v and ammonium citrate at 2% w/v[418]. The first chemical reduces the corrosion product while the second one chelates the iron salts. Similar solutions use concentrations of 2 and 2% w/v respectively[419]. MacLeod *et al.* suggest that heating and stirring accelerate the removal of salts during treatment[420].

#### 5.3.2.4. REMOVAL OF CHLORIDES

- **From the wood**

Two treatment options have been found in the literature for the removal of mineral salts from the wooden part of a composite.

The first one is based on successive immersion in deionized water[421]. As mentioned before, the type of water used depends mostly on the amount of chlorides that will be released and on the cost of producing the water. The bath should be changed often or a "cascade" of water can be done with boxes at different level, to provide circulation to the water.

The second suggestion is to soak the artifact in a sodium sesquicarbonate solution (2.5 to 5%w/v in water)[422]. This method is often cited in the Hawley's review about composites treatments. It seems to be used by conservators for removing a wide variety of salts. However, the alkaline pH of such solutions is a concern since organics are sensitive to these solutions as seen in the related section. Also,

[414] MacLeod *et al.*, 1989, p.245; Degrigny et Guilminot, 2000, p.7.

[415] See chapter 3.3.1.1, and 5.2.

[416] Degrigny et Guilminot, 2000, p.6.

[417] De La Baume, 1990, p.251; Degrigny et Guilminot, 2000, p.7.

[418] MacLeod *et al.*, 1991, p. 130-131; MacLeod *et al.*, 1994, p.206-208.

[419] Degrigny *et al.*, 2002, p.405.

[420] MacLeod *et al.*, 1991, p.119.

[421] Degrigny et Guilminot, 2000, p.7.

[422] Hawley, 1989, p.235-238.

like all alkaline or acidic treatments, if used, it should be for a very little time and followed by thorough rinsing[423].

- **From the metal**

Two popular treatments for removing salts from the metallic part of a composite are cited by specialists.

The first one is an aqueous solution of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 at neutral pH proposed by MacLeod *et al.* (method also proposed as storage solution). The addition of an inhibitor to the mixture should not be forgotten though. This treatment presents good results for the removal of chlorides from carbon steel and grey cast iron[424]. As seen before, the wood impregnation is also started with this process.

Another possibility includes an electrolytic technique such as the one designed by the team at the Arc'Antique laboratory (Nantes, France)[425]. In order to avoid an alkaline pH that would damage the wood, a neutral electrolyte of 1% (w/v) potassium nitrate in reverse-osmosis water was used[426]. As for electrolytic reduction, the treated artifacts were placed in a stainless steel anode cage while the artifact is made the cathode. A potential of -1.3V/ESS (mercury sulphate reference electrode) was applied to the metal[427]. Good results were observed and this technique was applied to several artifacts in this lab[428]. The amount of chloride in solution was checked every week and the electrolyte changed when needed. For 18 rifles treated in the same bath, six months of polarization were needed to obtain a satisfactory chloride extraction[429]. Two further points should be mentioned:

- due to corrosion of iron in neutral pH, the artifact should be immersed at the last minute and the potential applied immediately[430];

- due to the steady increase of the electrolyte pH during the polarization, a small amount of nitric acid is regularly added to the solution.

#### 5.3.2.5. RINSING

After any of the treatments cited above, artifacts should be rinsed thoroughly to remove all trace of chemical either in the metal or wood. To achieve a satisfactory rinsing, cathodic polarization at a

[423] De La Baume, 1990, p.251.

[424] MacLeod *et al.*, 1994, p.208.

[425] Degrigny *et al.,* 2002, p.404.

[426] *Ibid.*; Memet and Tran, 2005, p. 444.

[427] Degrigny *et al.,* 2002, p.404.

[428] Berger, 2004a, p.101; Memet and Tran, 2005, p.444.

[429] Memet and Tran, 2005, p.444.

[430] Berger, 2004a, p.101.

potential between -1.1V/ESS and -1.3V/ESS, in deionised water, was used at Arc'Antique for the rifles treatment[431].

### 5.3.3. Impregnation and consolidation of wood component

Numerous treatments have been tested during the last thirty years in order to optimize the consolidation of the organic part of composites. Before discussing these treatments and in order to understand why PEG cannot be applied by itself on composite artifacts, the mechanisms of iron corrosion in PEG mixtures will be explored.

#### 5.3.3.1. IRON CORROSION IN PEG

A complete electrochemical study of the behavior of iron in PEG solutions has been performed by Guilminot during her PhD. This study was part of her research about the action of iron corrosion inhibitors in PEG 400 mixtures[432].

The results indicate that *"iron corrosion was highest in the 20% PEG 400 solution due to the dynamics between the evolution of acidity, dissolved oxygen content and the adsorption and chelating properties of PEG in solutions"*[433]. These parameters are interrelated:

- the acid-alkaline reactions influence the conductivity;
- the solution is more conductive when PEG concentration is between 10 and 30%;
- the more conductive the solutions, the more adsorbed it is on the metal;
- the dissolved oxygen decreases when the solution concentration increases[434].

The next graphic presents pH variations versus PEG concentration (fig. 19).

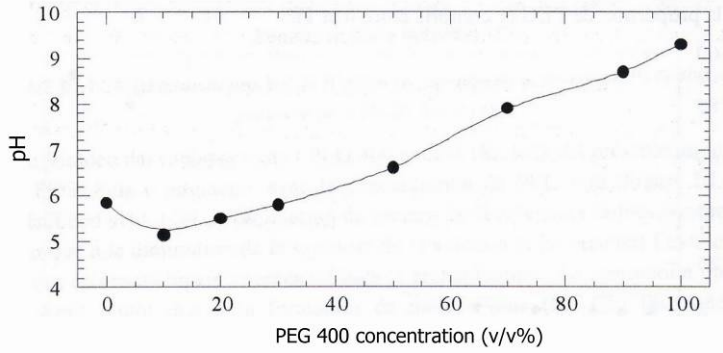


Figure 19: pH versus the concentration of PEG 400 solutions, at 25°C. From Guilminot, 2000, p.28.

*"PEG adsorption at the metal surface constitutes the first step in the iron corrosion mechanism. Iron (ions)/PEG complexes are then formed and diffuse into solution"*[435]. The corrosion is localized.

[431] Degrigny *et al.*, 2002, p.405; Memet and Tran, 2005, p.444.

[432] Guilminot, 2000, p.55-82.

[433] Guilminot *et al.*, 2002, p.2199.

[434] Guilminot, 2000, p.50 and 79.

[435] Guilminot *et al.*, 2002, p.2199.

Guilminot noticed that this localized corrosion is due to impurities contained in the metal (manganese sulfides in her case)[436].

If 20% v/v PEG 400 is the most corrosive solution to metal, solutions with concentrations up to 90% are all harmful. For 70% solutions, Guilminot noticed a dynamic between dissolved oxygen amount, pH and PEG adsorption at the surface of the metal resulting in a significant decrease of corrosion. PEG becomes almost benign to metal in concentrations greater than 90%[437]. The issue for conservators is that a 20%v/v PEG 400 solution is widely used for wood consolidation[438].

The fact that iron corrodes in PEG solution is also the reason why the Swedish ship *Vasa* has become a key study case in conservation. The vessel, mostly made of wood and iron, has been treated with PEG for almost twenty years[439]. Before that, the PEG method had not been tested on a large scale and the *Vasa* was the first large object on which PEG was used[440]. Also, since iron is a catalyst of the production of sulfuric acid (see chap.3.3.1.2), and because sulfur was present in the wood structure, all conditions were respected to encourage acid generation. At that point, as the summer 2000 was very humid, the relative humidity of the museum became higher than 60%. This initiated the formation of tons of acid, noticed by conservators six months later. To date, scientists and conservators are still working on an appropriate way to neutralize the acid[441].

This example emphasizes that PEG solutions should no longer be used on its own to consolidate waterlogged wood in contact with iron[442]. To get rid of this issue, the following options have been considered:

- the use of non aqueous solutions;
- the use of water-soluble polymers with inhibitive properties;
- the addition of a corrosion inhibitor in PEG solution;

The remainder of this chapter discusses the different treatment options tested so far.

#### 5.3.3.2. AN ALTERNATIVE TO PEG: NON AQUEOUS SOLUTIONS

The electrochemical processes involved in corrosion are retarded in the absence of water and especially in non-polar solvents[443]. Hence, the use of non aqueous solutions seems to be a worthwhile alternative to PEG.

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[436] Guilminot, 2000, p.78-79.

[437] Guilminot, 2000, p.76-79.

[438] Degrigny et Guilminot, 2000, p.8.

[439] Sandström *et al.*, 2003, p.20.

[440] *Ibid.*, p.19.

[441] Sandström *et al.*, 2002a and b; Sandström *et al.*, 2003; Fors and Sanström, 2006.

[442] Also introduced in chap.1 and 3.4.2.

[443] Cook *et al.,* 1985, p.148. Chap. 4.4.4.2 also mentions that sea-recovered iron can be dried through an immersion in water soluble solvents.

- **Resin and wax**

The acetone-rosin method cited in chap.3.4.2 has been often used on iron/wood composite artifacts[444]. In the early 1980's, this treatment was frequently applied in USA, Scotland and England[445]. Despite the fact that conservators sometimes noticed poor impregnation and highly brittle objects after treatment[446], the limitation of this method are the hazards associated with treating large artifacts[447]. One treatment also proposes heating the acetone to 52°C in an explosion-proof oven[448]. As a result, the acetone-rosin treatment might be a suitable option for small objects but not for large one.

The alcohol-ether method has also been used on small composites. A published example is the case of a Late Bronze Age sickle from England made out of a wood handle and a copper alloy blade[449]. The two parts could not be separated. The author considered ten different methods before choosing the alcohol-ether method[450]. Though interesting, this process is also incompatible with large artifact treatment since ether is highly flammable (chap.3.4.2).

In the same article, the author mentioned the cellusove-petroleum method as a possible treatment. This method was developed in England but no other citation has been found in the literature[451]. The advantages described by Brysbaert are that it is fast and uses less solvent than other methods. The drawbacks cited include health and safety issues and the rarity of treated artifacts[452].

Another treatment of metal/wood composites mentioned by Cook *et al.* is the butanol/PEG 3350 impregnation[453]. Again, for safety reasons, this type of treatment is not recommended on large artifacts. The PEG 3350 suggested by the authors is justified when the artifact is heavily damaged[454]. If the artifact is only mildly damaged, it is not necessary to soak an artifact in this solution. The pH of this solution is not mentioned by the authors.

Hawley cites a treatment used in New Zealand in the early 1980's: *"[…] the pistol[455] was dehydrated through alcohol baths. To the last bath, a mixture of beeswax, dammar resin, carnauba wax and paraffin was added. The mixture was heated to 60°C and as the alcohol evaporated, more*

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[444] Cook *et al.*, 1985, p.148; Hawley, 1989.

[445] Hawley, 1989. An alternative with iso-propanol instead of acetone is also proposed (Hawley, 1989, p.235).

[446] Chap.3.4.2; Grattan and Clarke, 1987, p.187.

[447] Cook et al., 1985, p.148.

[448] Hawley, 1989, p.231.

[449] Brysbaert, 1998 ; Brysbaert, 1999.

[450] *Ibid*.

[451] It is not precise, in the article, whether or not this pistol was made of iron and wood.

[452] Brysbaert, 1999, p.175-176.

[453] Cook *et al.,* 1985, p.148. It is not précised, in the publication, whether or not this solution was tested on ion/wood composites specifically.

[454] See chap.3.4.2.

[455] No mention was made of the type of metal involved (iron or not?).

*wax was added"*[456]. After twenty-four hours, the artifact was removed and cleaned of the excess of wax. Ten years after this treatment, the pistol still seemed in very good condition[457]. In terms of materials used, it is an unusual treatment.

- ***In situ* polymerization**

The Arc Nucléart© *in situ* polymerization method has been tested on iron/wood composites since the 1980's[458]. Although irreversible, it is currently used when no better alternative has been found[459]. The rifles mentioned in chap.6.2.1 and 6.2.3.2 were consolidated with this method because sulfur was detected in the artifacts with SEM-EDS analysis. In consultation with their client, Ephèbe museum, the scientists and conservators used this method to prevent degradation due to sulfuric acid despite its irreversibility[460]. This approach is interesting but it is not yet applicable on large composites. The drawbacks mentioned in chap.3.4.2.4 still hold: solvents are used which lead to safety issues, and the irradiation chamber needed is of limited size.

- **Supercritical $CO_2$**

Iron/wood artifacts have also been treated with supercritical carbon dioxide by Kaye *et al.*[461]. The first composites treated successfully by the team were sword handles made of wood, iron, gold and silver. The advantages of the method are that it is relatively quick, does not require any consolidant and that water in the artifact is rapidly replaced by methanol[462]. The presence of lead in an artifact presents an issue because methanol dissolves the lead oxide, thus increasing corrosion. Supercritical $CO_2$ may also react with lead oxide to form lead carbonate. A sacrificial anode should be set up if lead is present in an artifact[463].

The authors underline that large artifacts may require a consolidant to improve the strength or plasticity of the wood. A study on the topic is so far incomplete[464]. The limitations are similar to those of other treatments: solvent use may be a safety issue for large artifacts, and the equipment cost is extremely high[465].

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[456] Hawley, 1989, p.239.

[457] Hawley, 1989, p.239.

[458] *Ibid.*, p.237.

[459] Memet and Tran, 2005, p.447.

[460] *Ibid.*, p.447.

[461] Kaye *et al.*, 2000, p.239-241.

[462] *Ibid.*, p.239.

[463] *Ibid.*, p.240.

[464] *Ibid.*

[465] *Ibid.*, p.247.

#### 5.3.3.3. AQUEOUS CONSOLIDATION SOLUTIONS AND CORROSION INHIBITORS

Alternatives to solvent based treatments for composites have been studied since the early 1980's. This chapter is a chronological review.

Cook *et al.* from the Canadian Conservation Institute (CCI) initiated a series of trials which evaluated aqueous treatments for wood combined with brass, bronze, copper, lead and mild steel. Their first idea was to find *"water soluble resins, with the same basic structure as PEG, but altered so that they contained functional groups that would give corrosion inhibitive properties to the resin. The search focused on resins with amine functional groups because some long-chain organic amines were known to be effective corrosion inhibitors"*[466]. The resins chosen for iron/wood artifacts were Pluracol 824® (Aromatic amine polyol[467]) and Deriphat 151C® (N-coco beta amino propionic acid).

In parallel, they also tested the addition of the corrosion inhibitor Hostacor KS1®[468] in PEG 400 solution to protect the metal while impregnating the wood. Hostacor KS1® is a triethanolamine (TEA) salt of Hostacor H, an arylsulphononamido carboxylic acid[469] (fig.20). Hostacor® acts as an anodic inhibitor through the adsorption of its carboxylate and amido groups at the surface of the metal[470]. This inhibitor was recommended by the manufacturer, Hoechst, because it was designed as an additive in automobile antifreeze, another glycol solution[471]. The first results of Cook *et al.* showed good efficiency of Pluracol 824® at 15%v/v and Hostacor KS1® at 7%v/v in PEG 400[472].

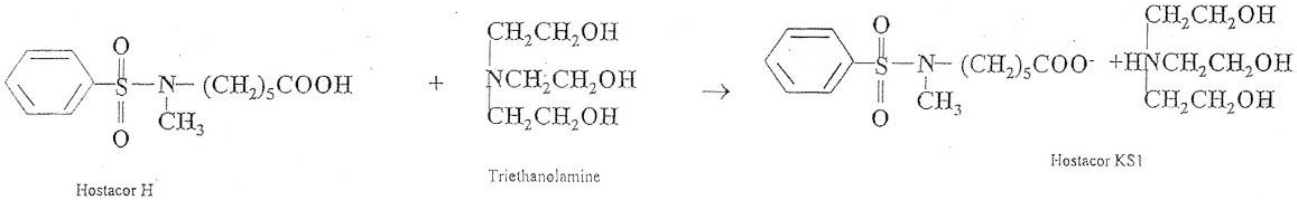


Figure 20: Chemical reactions leading to the formation of Hostacor KS1. From Argyropoulos *et al.*, 1999, p.50.

Based on these results, a complementary study measured the corrosion rate of metals in these new solutions through standard weight lost tests[473]. The trials were performed on bare metal surfaces[474]. The preliminary results for iron, presented by Gilberg in 1987, showed that PEG 400/Hostacor KS1®

[466] Cook *et al.*, 1985, p.148; Binnie and Selwyn, 1991, p.2.

[467] i.e. polyethylene glycol modify with melamine (Degrigny et Guilminot, 2000, p.8).

[468] Hostacor KS1 is an alkanolamine salt of an aryl(sulphon)-amido carboxylic acid (Selwyn *et al.,* 1993, p.182).

[469] Argyropoulos *et al.*, 1999, p.49. The aim of adding TEA in Hostacor® is to make the inhibitor soluble in water (same reference).

[470] Argyropoulos *et al.,* 1999, p.49. See also chap.4.4.1.3 for inhibitor definition.

[471] Cook *et al.*, 1985, p.151.

[472] *Ibid.*, p.158.

[473] Gilberg *et al.,* 1989; Selwyn *et al.,* 1993.

[474] Selwyn *et al.,* 1993, p.180.

offers better protection than Pluracol® against corrosion while treating the wood[475]. Selwyn *et al.* also published later results of the same study, adding lead and copper alloy/wood composite artifacts to the test samples[476]. At the time, the authors stated that more work was needed to determine how effective the solutions are on corroded metals[477]. Figure 21 shows the summary of results, for iron, from the CCI trials.

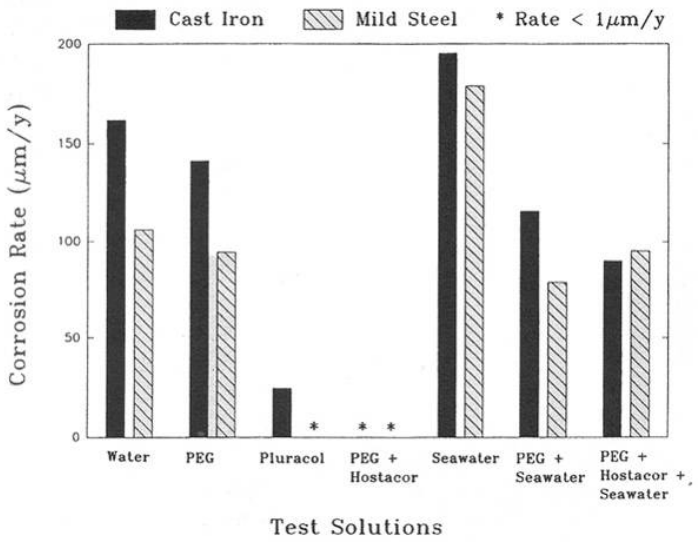


Figure 21: Bar chart of the average corrosion rates for mild steel and cast iron in the solution tested by the CCI team. From Selwyn *et al.*, 1993, p.187.

In 1997, Hoechst changed the Hostacor KS1® molecule to another one, more biodegradable, Hostacor IT®[478]. Hostacor IT® is a TEA salt of Hostacor IS, an acylamido carboxylic acid (fig.22)[479]. This change necessitated further tests to assure the performance of the new formula. This evaluation was undertaken in France by Argyropoulos *et al.* at the end of the 1990's. The experiment included different concentrations of PEG 400 and 4000 with 1%v/v of both Hostacor® inhibitors. The solutions were tested on wrought iron and their efficiencies compared through electrochemical analysis ($E_{corr}$/time and potentiodynamic curves[480]). The conclusion was that Hostacor IT® is as efficient as Hostacor KS1® in PEG solutions[481].

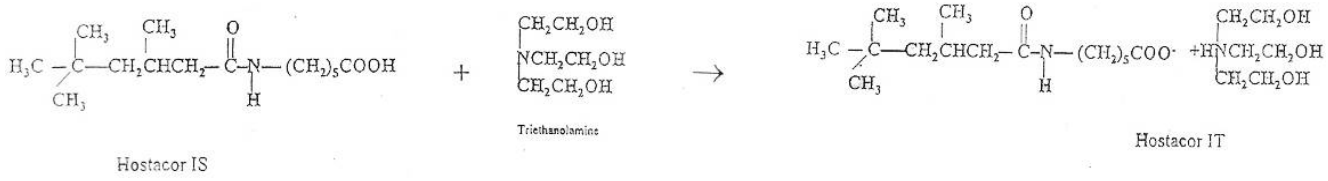


Figure 22: Chemical reactions leading to the formation of Hostacor IT. From Argyropoulos *et al.*, 1999, p.50.

[475] Gilberg *et al.,* 1989, p.267.

[476] Selwyn *et al.,* 1993.

[477] *Ibid.*, p.180.

[478] ICOM-WOAM, 1997, p.4.

[479] Argyropoulos *et al.*, 1999, p.50.

[480] See chapter 8 for the electrochemical analysis.

[481] Argyropoulos *et al.,* 1999, p.55.

At the end of the 1990's, other treatment options were explored in England. The study by Brysbaert on the treatment of an Iron Age sickle considered the following water soluble alternatives to PEG[482]:

- an impregnation with a polyalkylenglycol (PAG), which is less hygroscopic and less likely to form complexes than PEG[483]. Different PAG have been tested for conservation purposes[484]. One of them, Breox 50WPAG® has showed promising results for iron/wood composite treatment. It was used as an initial impregnation material, prior to PEG 4000[485]. Unfortunately the PhD dealing with this material as well as related publications were not found[486]. It is therefore difficult to discuss the precise treatment and its outcome. However, according to Guilminot, though PAG is less aggressive to metal than PEG, a corrosion inhibitor is likely needed during treatment[487]. The original work should be consulted in order to have more details. Additionally, it seems that PAG has not had a great following in conservation since the tendency of conservation was to simplify impregnations by using one type of polymer only (PEG 400 followed by PEG 4000 instead of PAG followed by PEG 4000). It is one of the reasons why Breox has not been more developed.

- the use of vapor phase inhibitors in PEG for composites was also cited by Brysbaert but the reference has not been found either[488]. The drawbacks, as for all inhibiting systems, are that long term effects of the inhibitor on organics are unknown and that the interface between metal and wood is not well protected[489].

In 2000, an electrochemical study demonstrated that the corrosion state of the metal dictates the concentration of Hostacor® in PEG solution necessary for successful treatment[490]. Bobichon *et al.* recommended that a 5%v/v solution of Hostacor IT® should be used on corroded metal, while, a 1%v/v solution is sufficient for non corroded metal[491]. Newer research showed that *"for higher*

[482] Brysbaert, 1999, p.175-176.

[483] PAG's molecules are slightly longer than PEG (presence of propylene instead of ethylene) and their –OH groups have different orientations than PEG. This combination provides less corrosive properties (Guilminot, Conservation Scientist, Arc'Antique, France, written communication, July 2007).

[484] Breox 50WPAG®, -50A20®, and -50W200® (Pournou *et al.,* 1999, p.105; Degrigny et Guilminot, 2000, p.8).

[485] Degrigny et Guilminot, 2000, p.8.

[486] Degrigny and Guilminot (2000) mention the following PhD: Dean, L.R.. *The conservation and treatment of ancient waterlogged wood with polyalkylene glycols and the diffusion of water-borne polymers through wood.* PhD Thesis, University of Portsmouth, 1993.

[487] Guilminot, written communication, July 2008.

[488] Brysbaert (1999) cites: Payton, R. The stabilization and conservation of a complex composite object. In ICOM, Committee for conservation. Working group on wet organic archaeological metarial. Newsletter, 18, p.3-4. Hawley, p.223-243.

[489] Brysbaert, 1999, p.175-176.

[490] Bobichon *et al.,* 2000, p.145.

[491] *Ibid.*, p.151.

*concentrations of Hostacor IT* [greater than 1%]*, one has problems of viscosity of the solution and thus of penetrability in the corrosion products"*[492].

Also in 2000, Guilminot presented her comparison on the efficiency of tannins, phosphates and Hostacor IT® in PEG solutions. It showed that tannins are less inhibitive than Hostacor® and that phosphates seemed promising but required further study[493]. This research also proposed a model describing Hostacor IT®'s action on metal: carbon chains of Hostacor® are positioned perpendicular to the iron surface and constitute a hydrophobic barrier limiting solvent penetration (water from PEG solution); Hostacor® molecules thereby form a compact, thin, and very adherent film on the surface. This phenomenon only occurs, in PEG solution, when Hostacor® concentration is high enough to increase the pH of the solution above 5.5 (1%v/v is enough)[494]. Despite the measured efficacy of Hostacor IT®, several drawbacks have been noted over the years:

- the action of the inhibitor on organic compounds is not known. More research needs to be performed in this field[495];

- Hostacor IT® is biodegradable, leading to a decrease in effectiveness over time and a significant development of microorganisms[496]. Lemoine underlined that biocides should not be used with Hostacor® because they are unstable at the pHs of the solutions[497]. However a recent study showed that Hostacor® is compatible with the biocide Dowicide®[498];

- the presence of chlorides reduces the effectiveness of the inhibitor[499]. As discussed in chapter 6.1, an adsorption competition takes place between $Cl^-$ anions and Hostacor® molecules at the metal surface[500]. Recent research showed that the amount of chloride should stay below 900ppm in the solution to avoid this issue (with 1%v/v Hostacor®)[501]. It also reinforces the importance of removing mineral salts from an artifact during the first steps of treatment;

- the metal/wood interface is difficult to protect[502]. The accessibility of Hostacor® to the metal can be limited because the inhibitor molecules are too large to pass through the wood[503]. A study suggests that the lack of oxygen at the wood/metal interface could also limit the inhibitor action[504].

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[492] Memet and Tran, 2007, p.452.

[493] Guilminot, 2000, p.156-157.

[494] *Ibid.*, p.126-127.

[495] Guilminot *et al.*, 1998, p.241; Lemoine, 2000, p.41; Degrigny, oral communication, 12/07.

[496] Argyropoulos *et al.*, 2000, p.254; Memet and Tran, 2005, p.450-454.

[497] Lemoine, 2000, p.41.

[498] Memet and Tran, 2005, p.453 and chap.5.3.1.2.

[499] Guilminot, 2000, p.157; Memet and Tran, 2005, p.450-454.

[500] Guilminot, 2000, p.157.

[501] Memet and Tran, 2005, p.452.

[502] Guilminot, 2000, p.157.

- another significant drawback of Hostacor® is that conservators are at the mercy of the manufacturer's decision to change the formula of their compounds. The shift from Hostacor KS1® to Hostacor IT® in the 1990's is here a good example. Today it appears that Hostacor IT® is no longer available in the US and currently difficult to obtain in Europe[505]. Therefore it seems worthwhile to test other inhibitors in PEG solutions. These new inhibitors should be readily available, independent of a patent, easy to prepare, to use, and be safe and affordable. Also, since Hostacor IT® is the best studied corrosion inhibitor employed for iron / wood composites, it constitutes a perfect benchmark for comparing new inhibitors. This is why Hostacor IT® is used in the present work[506].

### 5.3.4. Drying

The drying techniques discussed in chap.3.4.3 are also applicable on composites.

Freeze-drying is a good method if the artifact is small enough to fit in the apparatus and the treatment based on aqueous solution. If the artifact is too large for the freeze-dryer, a controlled air drying can be carried out. Freeze-drying at atmospheric pressure is also possible for large artifacts[507].

The use of supercritical fluid is a promising method but requires further study to be properly adapted to wood and composites[508].

### 5.3.5. Post-treatment storage

The recommendations for long term storage of treated composites found in the literature are[509]:

- the light should not exceed 50 lux to avoid the development of microorganisms;
- the temperature should be maintained between 18 and 20°C;
- relative humidity should be stable, between 25% (below, the organic component might shrink) and 46% (the metal corrodes above this limit). This suggested RH is a compromise between ideal conditions of each material since wood should be kept between 55 and 60% and iron below 20% (see chapter 3 and 4). Also, especially for non-separable composites, because each material cannot be stored in ideal conditions, avoiding fluctuations of temperature and RH is fundamental. Again, if the RH

[503] Argyropoulos *et al.*, 2000, p.261; Guilminot, 2000, p.157.

[504] Argyropoulos *et al.*, 2000, p.261.

[505] The US Hostacor® supplier, Clariant Corporation, provides now another Hostacor named "Hostacor 2732". It has less amine (TEA) than Hostacor KS1 or IT® (Stephens, Business Manager, Clariant Corporation, written communication, July 2008). Hostacor IT® is still available in Europe but difficult to obtain too (Guilminot, written communication, July, 2008).

[506] Fortunately, it was not difficult to obtain the inhibitor for this study since TMM®'s laboratory has few liters left from a previous purchase.

[507] Degrigny et Guilminot, 2000, p.9.

[508] See chap.6.3.2.

[509] Brysbaert, 1999. Brysbaert's article concerns a copper/wood artifact.

becomes higher than 60% it may cause metallic salts to initiate the formation of sulfuric acids. This is a particular concern when artifacts have been treated with PEG that is hygroscopic (*Vasa*'s example)[510].

## *5.4. The gun carriages of the USS Monitor: an example of large and complex composites*

### 5.4.1. Description

Two gun carriages were specially designed for the USS *Monitor* between the late 1861 and early 1862[511]. They were recovered from the seabed in 2002 buried inside the rotating gun turret of the ship. The carriages were isolated for treatment in 2004. One of the ingenuous features of the carriages is their braking mechanism. It would operate by turning the braking wheel on the side of the carriage that would squeeze the bottom fins (iron friction plates) against the wooden guide beams on the floor of the turret[512] (fig.23).

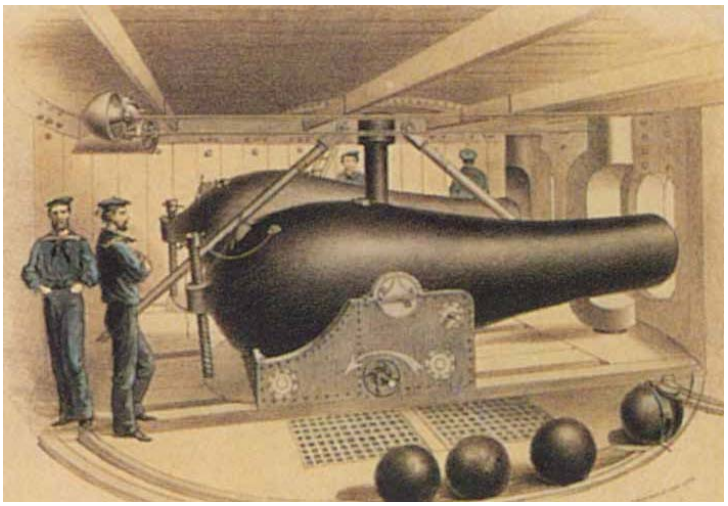

Figure 23: Drawing showing carriages in function. From TMM®.

Figure 24 is a view of one of the port side carriages in its treatment tank, at TMM®. Note that the artifact is still upside down as they were found when excavated from the turret[513].


Figure 24: Port carriage of the USS *Monitor* in its tank. From TMM®.

The carriages are large and complex composites made of hundreds of individual components including waterlogged wood, copper alloy, wrought iron, cast iron, and steel[514]. On each carriage, cast iron side-plates sandwich 4 inch wooden cores and the layers are held together with seven 1 inch bolts[515].

[510] Degrigny et Guilminot, 2000, p.9. See also chap.3.3.1.2 and 5.

[511] Schindelholz and Krop, 2004.

[512] Secord, oral communication, May 2008.

[513] The Mariners' Museum®, USS *Monitor* Center, 2004.

[514] The Mariners' Museum®, Conservation Department, 2007. The presence of steel is suggested by conservators but has not been proven yet (Nordgren, written communication, August 2008)

[515] Schindelholz and Krop, 2004.

Because the wood is so integrated with the metal structure, dismantling the parts for separate treatments might damage both the organic and the iron components. Additionally, recent data affirmed the presence of sulfur in wood recovered from the *Monitor*[516]. For these reasons, the long term stabilization of these carriages is a considerable challenge for the conservation team.

At the beginning of 2007, the iron braking plates presented a particularly high rate of corrosion. Referring to the original construction plans of the carriages, conservators found that the iron friction plates were connected to the brass brake wheels via an iron axle and screw device creating a galvanic couple[517]. As a result, the first conservation treatment performed on these pieces was the removal of the accessible copper alloy parts[518].

The carriages were later placed under impressed current in tap water[519] to limit further corrosion. A traditional immersion in sodium hydroxide would have accelerated the wood degradation so NaOH was avoided.

### 5.4.2. Discussion of possible treatments

#### 5.4.2.1. Removing mineral salts from the metal

Removing mineral salts from the metallic part can be performed electrochemically, with the Arc'Antique method, i.e. electrolysis in a neutral solution of 1% (v/v) potassium nitrate, as discussed in section 5.3.2.4.

A solution of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 at neutral pH, proposed by MacLeod *et al.*, is an alternative extraction medium but requires an inhibitor[520]. This treatment can be overly aggressive to metals since ammonium citrate is a powerful chelating agent for metal ions. A specialist in the use of this chemical classes the affinities of ammonium citrate with ions as follow[521]: $Cu^{2+}$> $Fe^{3+}$> $Al^{3+}$> $Pb^{2+}$> $Zn^{2+}$> $Ni^{2+}$> $Fe^{2+}$.

#### 5.4.2.2. Wood treatment

Removing metallic salts from the wood could be very difficult because there are few exposed wood surfaces on the carriages. Any chemical used for that purpose will have to be thoroughly rinsed from the artifact to avoid post-treatment degradation of the iron due to residual chemicals.

Removing chlorides from the wood can be done in parallel with chloride extraction from the metal. Since the carriages have been isolated from the turret, the release of chlorides from the artifact, into tap water, has been regularly monitored.

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[516] Grieve, oral communication, January 2008

[517] The Mariners' Museum®, Conservation Department, 2007.

[518] *Ibid.*

[519] Tap water of the city of Newport News usually count between 20-25mg/l of chlorides and its pH vary from 7.3 to 7.8 (Nordgren, written communication, August 2008)

[520] MacLeod *et al.*, 1994, p.208 and chap.6.2.4.

[521] Mansmann, 1998, p.222.

The consolidation treatment of the wooden components is a more delicate problem. A solvent based treatment is not feasible for safety reasons because the pieces are too large and would require immersion in large volumes of solvent. A water soluble option appears more appropriate. Referring to the previous chapter about PEG alternatives for composites[522], the following treatments can be considered:

- use of PAG;
- vapor phase corrosion inhibitor in PEG;
- PEG with a corrosion inhibitor in solution.

To date, the lack of documentation about PAG as well as about vapor phase inhibitors limits their potential use.

The addition of a corrosion inhibitor to PEG solutions seems more feasible since it is more widely practiced. The choice of the inhibitor is open to discussion. If TMM® has sufficient supplies of Hostacor IT® to treat the entire artifact, it could be used with full knowledge of its drawbacks. Also, depending on the results of this study, sodium nitrite, carboxylatation solution or sodium decanoate could be considered as well. Complementary research should be performed to assess the effect of the chosen inhibitor on wood.

#### 5.4.2.3. DRYING

Because of the significant size of the carriages, the drying process should be either an atmospheric freeze-drying or a controlled air drying.

#### 5.4.2.4. POST-TREATMENT STORAGE

A good storage environment will be the key to the long term stability of these artifacts. The recommendations made in chapter 6.5 should be considered. Particular attention should be paid to the RH of the storage or display environment since excessive RH can lead to acid formation in the presence of iron and sulfurs[523].

[522] Chap.6.3.3.

[523] At TMM®, storage conditions of Monitor's artifacts are: RH between 45 and 55%, temperatures between 70 and 71°F. From Heaton, TMM®, October 2008.

# 6. Synthesis and perspectives of current research

Reviewing published literature and accepted practices about waterlogged wood and marine iron artifacts allowed a better understanding of current approaches to non-separable composites. Due to the complexity of such artifacts, specific treatments for each material have been combined to create treatments for composites.

The significance of storage solutions have been underlined several times since artifacts might stay a long time soaked prior and during treatment. Several possibilities of storage are proposed in the literature, and discussed above. The meticulous documentation and deconcretion of composites were also described in chapter 5.3.2.

The issue of removing metallic salts from wood is highly dependent on the condition of the wood. If it has been almost mineralized, removing iron might result in weakening its structure. The presence of sulfur in the organic part will also guide this treatment step. If no or very little sulfur has been detected by analysis in the wood, removing iron salts might not be needed. This is also the case if the future storage environment is carefully controlled.

On the other hand, the removal of chlorides from any artifact is universally accepted to be beneficial to its long term stability. Indeed, as the metal is stuck to the wood, the post treatment storage has to be slightly adapted to the wood to avoid its shrinkage. Yet, as seen in the "iron" section, akaganeite can be formed at very low RH levels. This is why chloride removal is so important. An electrochemical treatment designed to remove chlorides from composites, in neutral solution, has proved to be effective for that purpose (chapter 5.3.2.4).

A thorough rinsing of the artifact should follow any of these preliminary steps.

Consolidation treatments for the wood components of composites were discussed. A summary of materials, methods and noteworthy issues follows:

- PEG is the most commonly used treatment to consolidate waterlogged wood but is corrosive to metals;
- solvent based impregnation is applicable to small artifacts but not to large ones;
- water soluble impregnation polymers, such as Pluracol 824®, that should inhibit corrosion, are not sufficiently protective of the metal component;
- a mixture of PEG plus corrosion inhibitor is a preferred treatment method;
- Hostacor IT® is the most widely used corrosion inhibitor with PEG solution;
- the variable availability of Hostacor IT® is one of its significant limitations.

Lastly, ambient and vacuum freeze-drying as well as post-treatment storage of composites have been discussed.

The formula changes in Hostacor IT®, as well as its other limitations, require investigation into new corrosion inhibitors to be used with PEG. The upcoming treatment of the USS *Monitor* gun carriages is a good example of artifact which can benefit from the study of other inhibitors.

The second part of this thesis is devoted to investigating the effectiveness of several inhibitors in PEG solution. As mentioned in the introduction, recent studies about "green" inhibitors, presented the opportunity to test environmentally friendly chemicals. Some of the inhibitors investigated are carboxylate based solutions as researched by the *Laboratoire de Recherche des Monuments Historiques* (LRMH, France)[524]. Another corrosion inhibitor selected is sodium nitrite. TMM® has been considering its effectiveness for a number of years as part of a collaboration with CC Technologies (CCT), a corrosion engineering firm[525]. Chapter 8 describes the experimental procedure, sample materials and solutions used for this study.

[524] More recent results are in: Hollner *et al.,* 2007a and b.

[525] Nordgren *et al.*, 2007, p.59.

# *Part II: Effectiveness of corrosion inhibitors in PEG solutions: experimental protocol and analytical methods*

# 7. Materials and method

As mentioned previously[526], after reviewing the literature about non-separable waterlogged wood/iron artifacts, we were interested in studying the effect of Hostacor IT®, sodium nitrite, carboxylatation solution, and sodium decanoate in PEG solution, both on bare and corroded carbon steel samples.

The metal chosen and sample preparation are described in the first section of this chapter. The solutions used, their properties and the specific concentrations employed are discussed in the second part. The experimental protocol, including an overview of the analytical methods, is the topic of the third section of the chapter.

## *7.1. Reference material*

### 7.1.1. Bare carbon steel

These samples were called "bare" samples, i.e. non-corroded, in contrast to the second group of coupons that were naturally pre-corroded (see next chapter). The composition of this metal has been determined through analyses. An overview of the analytical methods used for this purpose and the results can be found in appendix 1. These analyses showed that bare samples are made from a low carbon steel (very similar to AISI-SAE « 1011 »)[527].

### 7.1.2. Analogue material: corroded carbon steel

To best represent marine archaeological artifact conditions, naturally corroded iron in seawater was first selected as analogue material. Owing to good relationships between TMM® and the US Navy, Navy divers were able to provide steel from a wreck that was submerged for at least five to ten years. Since, as discussed in chapter 4.2.2, the formation of corrosion products is rapid during the first several years[528], the age of the wreck was perfect for the study. Unfortunately, the metal recovered from the ocean was coated with a homogeneous paint layer. This sample was therefore discarded since the electrochemical behavior of the samples would not have been comparable to uncoated bare samples[529]. Following further requests for available material that could not be filled, it was finally decided to find a

[526] See chapters 1 and 6.

[527] AISI is the acronym for "American Iron and Steel Institute-Society of Automotive Engineers". SAE stand for the "Society of Automotive Engineers". A steel alloy designation system has been developed by these societies. Their websites are: American Iron and Steel Institute, 2008; Society of Automotive Engineers, 2008.

[528] Memet, 2007, p.159.

[529] Degrigny, written communication, January 2008.

material that has been naturally corroded outdoor (not underwater). As a result, steel was purchased from the Old Dominion Recycling junkyard of Hampton (VA) in January 2008 (fig.25).

Figure 25: Corroded carbon steel as purchased.

As bare material, this steel has been analyzed by the laboratory of Newport News's Shipyard but the results are not available yet (appendix 1).

The corrosion products were analyzed by XRD at ODU. The results show the presence of magnetite ($Fe_3O_4$), lepidocrocite ($\gamma$-FeOOH) and goethite ($\alpha$-FeOOH) which are common corrosion compounds (see chapter 4.2.1). These corrosion products developed both under and above a mill scale layer according to Dr. Cook observations[530].

As mentioned in chapter 5, adsorption competition between a corrosion inhibitor and chlorides at the surface of an artifact can diminish inhibition. This has proved to be the case for Hostacor IT®[531]. This phenomenon reinforces the need to remove mineral salts from an iron / wood composite prior to immersion in a corrosion inhibitive solution. For this study, since the amount of chlorides in the corroded material was unknown, a sample was soaked in 2% NaOH solution with deionized water and the release of chlorides into solution was monitored over time. After one week, the concentration of chlorides in the solution was still under 10ppm (appendix 2). Considering this low amount, it was concluded that there was no need to proceed with chloride removal from the corroded material[532].

### 7.1.3. Sample preparation

First of all, the size of the samples had to be chosen. In order to have comparable results from one sample to another, all samples should have the same size[533]. The bigger the coupon, the better observations one can make since on small samples, preferential corrosion of the edges might spread easily all over the surface of the coupons and lead to less accurate interpretation of corrosion phenomenon. Nonetheless, larger samples also involve more solution and larger jars, i.e. more

[530] A mill scale interface is an oxidation layer, consequence of the heat process of the metal production (hot rolling for example). It is composed of wuestite (FeO), magnetite ($Fe_3O_4$) and hematite ($\alpha$-$Fe_2O_3$). This oxidation layer can be between 50 and 100 µm thick. One of its particularities is that when its surface cracks, the corrosion develops outside and under the mill scale layer. Cook, oral communication, May 2008.

[531] Guilminot, 2000, p.157; Memet and Tran, 2004, p.452.

[532] If the chlorides amount of the solution is lower than 900ppm, Hostacor IT® remains effective (Memet and Tran, 2004, p.452).

[533] Degrigny, written communication, December 2007.

expenses. Therefore, in consultation with Degrigny, and guided by the width of the available material, the sample size became: 2.5x4.5x0.2cm.

The coupons were cut with a oil cooled circular saw. A hole was drilled in each sample to insure good electrical contact with the wire needed for future electrochemical measurements. Coupons were then degreased in an ultrasonic ethanol bath for one hour.

For consistency of sample surface and thereby for the reproducibility of the electrochemical measurements, the surface of the bare carbon steel samples required significant polishing[534]. A superficial corrosion layer was first removed with an iron brush on a hand-held Dremel®. Both sides of each sample were polished with SiC paper, with grit ranging from 180 to 1500. Grit selection and polishing techniques were performed in consultation with specialists and a Buehler® expert[535]. Afterwards, the samples were rinsed with ethanol in an ultrasonic bath for one hour.

In regard to the specific preparation of the corroded samples, after sawing the original material, the freshly exposed edges of the corroded samples were coated with an epoxy resin. This aims to avoid differential corrosion between the bare edges and the corroded main surfaces.

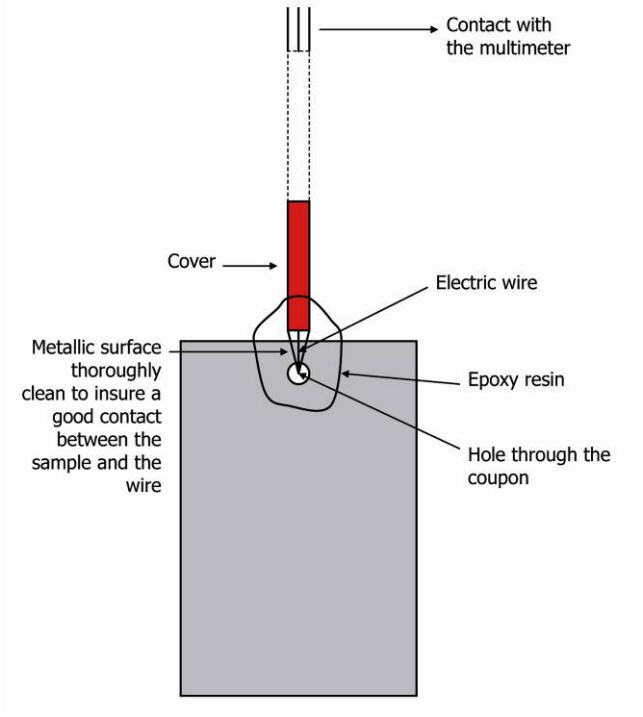


Figure 26: Sample connection system. From Degrigny, written communication, December 2007.

Copper electrical wires were then attached to the samples. Good connections on each sample were checked with a multimeter before sealing the wires on the coupons with an epoxy resin[536] (fig.26). The resin is also useful to avoid corrosion of the coupon/wire connection during the experiments.

Until the samples were ready to be tested, they were stored in a sealed polyethylene box, with silica gel, to prevent corrosion (fig.27).

[534] Hollner, PhD student, LRMH, France, oral communication, October 2007; Degrigny, oral communication, December 2007.

[535] Degrigny advised to polish until 1200 grit (oral communication, January 2008). Hollner, for her PhD, went until 4000 (oral communication, January 2008). Guilminot, also for her PhD, went until 1µm particle size on a polishing cloth (Guilminot, 2000, p. 11). 1500 grit is the compromise chosen here after these sources. The polishing machine used was a Buehler® MetaServe2000.

[536] Epoxy Systems®, Product #899, "A" resin Component and "B" Hardener Component.

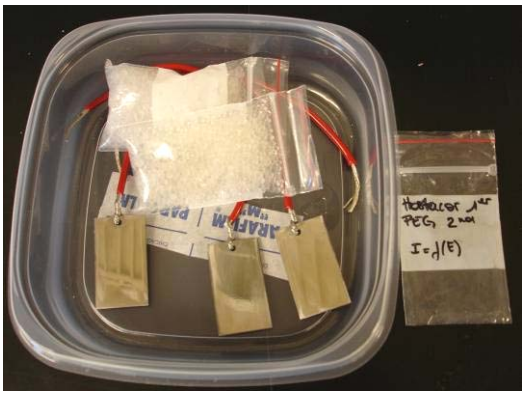

Figure 27: Bare samples drying, after gluing the coupon/wire interface. Silicagel is also in the box to prevent corrosion prior to trials.

## *7.2. Solutions*

### 7.2.1. PEG solutions

Guilminot's research on iron corrosion inhibitors in PEG solution, involved the use of PEG 400 solutions[537]. For this study and in order to have comparable data with Guilminot's research we chose too to test corrosion inhibitors in PEG 400 solution, rather than in another molecular weight. The concentration of PEG in each solution employed for these tests varied depending on the experiments performed. For the assessment of the inhibitors' effectiveness ($E_{corr}$ measurements, see chapters 1 and 7.3), a 20%v/v solution in deionized water was used since it is the most corrosive PEG 400 solution (see chapter 5.3.3). We assumed here that if the corrosion inhibitors are effective in the most corrosive solution, they should be effective too in less aggressive PEG concentrations as well. In the results part (chapter 8 to 15), when "PEG" will be mentioned on its own, it suggests that we are talking of a 20%v/v PEG 400 solution in deionized water.

To evaluate the long term effectiveness of the corrosion inhibitors (i.e. voltammetric analyses, see chapters 1 and 7.3), PEG concentration was also selected in accordance with Guilminot's study. The aim of these analyses was to reproduce the environment for a piece of metal embedded in PEG impregnated wood. Therefore, performing voltammetric measurements in 100%v/v PEG 400 electrolyte would accurately represent post-treatment conditions. Practically, measurements could not be taken in a 100%v/v PEG solution because the potentiostat required a slightly conductive aqueous electrolyte[538]. As mentioned in chapter 5.3.3, Guilminot observed several changes in 70%v/v PEG 400/water solution: the amount of dissolved oxygen decreased significantly, a higher electrolytic resistance was observed as well as a higher pH[539]. For these reasons, a 70% PEG solution was found to be a good compromise as being highly concentrated and aqueous at the same time. In agreement with Degrigny, a 70%v/v PEG 400 solution in deionized water was thereby chosen for this part of the study.

[537] Guilminot, 2000, p.6.

[538] Degrigny, written communication, April 2008.

[539] Guilminot, 2000, chap.III.

The PEG used for this project was purchased at the Spectrum Laboratory Services company[540]. A Material Safety Data Sheet (MSDS) is available in appendix 5 (CD-R).

The pH of the 70%v/v PEG 400 solution was 8.1. The pH of the 20% PEG 400 solutions varied between 5.3 and 5.6, which is comparable to Guilminot's results (see chapter 5.3.3.3). These slight variations may be related to small variations in the pH of the water supply or to the pH-meter accuracy[541]. Any pH change during trials was noted and reported in the result section.

### 7.2.2. Hostacor IT®

Composition and action of Hostacor IT® have been discussed in chapter 5.3.3.3. As suggested by Bobichon *et al.* a 5%v/v solution of Hostacor IT® should be used on corroded metals, while a 1% solution should be sufficient on non corroded metals[542]. These concentrations seemed therefore appropriate for this project. However Memet and Tran mentioned that a concentration higher than 1% increases the viscosity of the solution, lowering penetrability of the corrosion inhibitor into the corrosion products[543]. Based on this last observation, a 1%v/v Hostacor IT® solution, in deionized water, was employed for this study. Also, in the third part of this thesis (results part), when "Hostacor®" is mentioned, it generally means "1%v/v Hostacor IT® in deionized water". If not, this will be underlined. A chemical description sheet as well as a "public report" are available in appendix 5. The pH of 1%v/v Hostacor® in deionized water was 8.1. The pH was 8 when 20%v/v PEG 400 was added to the solution. This result is comparable to Guilminot's data[544].

As discussed in section 5.3.3.3, through discussions with the business manager of Clariant Corporation (the Hostacor® supplier in the U.S.) TMM® was told that Hostacor IT® was not available for purchase in the U.S. and has been replaced by "Hostacor 2732®"[545]. This new Hostacor® has the same composition as Hostacor IT® but is more concentrated and has no or very little triethanolamine salts (TEA)[546]. In other words, since Hostacor IT® is made by adding Hostacor IS® to TEA, Hostacor 2732® may be very similar to Hostacor IS® (see fig.22, chapter 5.3.3.3). For conservators, the removal of TEA from the chemical can be an issue since TEA salts were added to Hostacor® to raise its pH so that it becomes soluble in aqueous solution[547]. As a result, the new Hostacor® is not soluble in water (see Hostacor 2732® description sheet p.1, appendix 5). However, according to Clariant Corporation, any

[540] Appendix 3 provides names and details of suppliers of the chemicals employed for this study. For PEG 400, the Spectrum catalog number PO110, and its average molecular weight: 397.

[541] The pH-meter used was: Fisher Scientific Accumet Research AR25 Dual Channel pH/Ion meter.

[542] Bobichon *et al.,* 2000, p.151.

[543] Memet and Tran, 2007, p.452.

[544] Guilminot, 2000, p.97.

[545] Stephens, Business Manager at Clariant Corporation, oral communication to Nordgren, July 2008.

[546] *Ibid.*

[547] Argyropoulos *et al.*, 1999, p.49.

water soluble alkaline substance can be added to the new chemical, which is acidic, to neutralize its pH and make it soluble in water[548]. The supply company seems also able to purchase Hostacor IT® from Europe for U.S. clients if needed[549]. Nonetheless, at Arc'Antique, in France, where Hostacor IT® has been used for several years, it has recently been very difficult to obtain this compound from suppliers[550].

### 7.2.3. Sodium nitrite

As mentioned previously in the introduction and chapter 6, this corrosion inhibitor was suggested and tested for TMM®, by CC Technologies (CCT), to replace the highly alkaline sodium hydroxide storage solution used for large artifacts[551]. CCT trials compared $NaNO_2$, at neutral pH, with three other solutions: sodium hydroxide (NaOH, pH 12), sodium carbonate ($Na_2CO_3$, pH 10) and sodium molybdate ($Na_2MoO_4$, pH 9). *"Molybdate is a well known effective* [corrosion] *inhibitor that will not likely leave a long term film on the surface but could however present environmental concerns should the storage water be disposed of through the municipal sewer system. Carbonates, though environmentally friendly, could form a tenacious film that could be hard to remove. Of the candidates, nitrites might prove to be the best* […]*"*[552]. Their assessment was performed with electrochemical measurements[553] and demonstrated that when comparing these solutions, sodium nitrite showed optimal performances on iron, steel, brass and lead. On-going long term tests of $NaNO_2$ should prove if it significantly reduces galvanic corrosion[554].

Within the framework of this project, the advantages offered by this chemical are:

- its neutral pH (i.e. not aggressive to organics);

- the solution's concentration is very low[555] (100ppm, i.e. 100mg/l or $1{,}45.10^{-3}$M), involving less chemical handling and disposal;

- it is effective on several metals (iron, copper and lead), which is of interest when dealing with artifacts made of dissimilar metals.

The environmental effect of sodium nitrite is somewhat unclear. Depending on the MSDS consulted, it is either: *"very toxic to aquatic organisms"*, or *"if diluted with water, this chemical released directly or indirectly into the environment is not expected to have a significant impact"*[556].

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[548] Stephens, written communication, July 2008.

[549] Stephens, oral communication to Nordgren, July 2008.

[550] Guilminot, written communication, July 2008.

[551] CC Technologies, INC., 2007, p.57.

[552] *Ibid.*

[553] They used Linear Polarization Resistance (LPR) analysis, which requires the use of a potentiostat (Costa, 2003, p.89).

[554] CC Technologies, INC., 2007, p.57.

[555] Nordgren, written communication, December 2008.

The solutions made for this experiment are described below:

- 100ppm $NaNO_2$ in deionized water: pH 6.4 (pH of deionized water at 6.8);

- 100ppm $NaNO_2$ in 20% PEG 400, in deionized water: pH 4.4.

As for PEG and Hostacor®, when "sodium nitrite" will be mentioned in the results part this will suggest "100ppm $NaNO_2$ in deionized water".

### 7.2.4. Sodium carboxylates

*"For several years, the Laboratoire de Chimie du Solide Minéral (LCSM)* [Nancy, France], *has been studying sodium carboxylates with linear carbon chains as corrosion inhibitors for many metals: copper, zinc, iron, magnesium alloys and lead. These compounds are non-toxic and are derived from fatty acids extracted from vegetable oil (colza, sunflower and palm)"*[557]. Over the years, several corrosion inhibitor formulations have been developed and are nowadays used in industry as temporary protection of metallic pieces[558]. These solutions are based on sodium carboxylate, which has the general formulae of $CH_3(CH)_{n-2}COONa$, and is annoted $NaC_n$[559].

According to these results, the LCSM associated with the Laboratoire de Recherche des Monnuments Historiques (LRMH, France), performed several studies to improve the use of these corrosion inhibitors for the protection of cultural heritage artifacts[560]. On archaeological iron, the best results have been obtained with $NaC_{10}$. For bronze, $NaC_7$ is more effective[561].

On bare metal, the effectiveness of the solution is due to the formation of a nanometric layer of metal carboxylate (iron or copper carboxylates). The stability of this layer depends on the carbon chain length of the carboxylate anion[562].

On corroded metal, this metallic soap is less effective due to more heterogeneity in thickness and composition of the surface. A carboxylate derivative was designed to form a thicker protective layer on the metal[563]. The joint effect of a carboxylic acid and an oxidizing agent was found to be effective. Their combination enhances the release of iron cations which allow the precipitation of thicker iron

[556] The MSDS are available in appendix 5.

[557] Rocca and Mirambet, 2007, p.314.

[558] *Ibid.*

[559] Hollner *et al.*, 2007a, p.156; Hollner *et al.*, 2007b, p.65.

[560] The development of these corrosion inhibitors is part of the European PROMET project (Degrigny *et al.*, 2007, p.32)

[561] Rocca and Mirambet, 2007, p.326 and 331.

[562] Hollner *et al.*, 2007b, p.69; Rocca and Mirambet, 2007, p.331.

[563] The aim of this new formula was also to create a protective layer on artifacts that can be applied with a brush, i.e. with no need to soak the object (Hollner *et al.*, 2007b, p.66).

carboxylate layers[564]. These new formulae were named "carboxylatation solutions". They are mixtures of $H_2O_2$ or $NaBO_3$ as the oxidizing agent and $HC_{10}$ or $HC_{12}$ as the carboxylic acid[565].

For this project, $NaC_{10}$ solutions are of interest because their neutral pH might increase the pH of the 20% PEG 400 solutions rendering them harmless to organics. Additionally, as underlined in chapter 1, they are environmentally friendly, reversible, not costly, and easy to prepare. The drawback of sodium decanoate is that it cannot protect corroded material. However, the main advantage of the carboxylatation solutions is that they are effective on corroded iron. Their principle drawback is that the solution is acidic, which may increase the acidity of the PEG solutions tested here. Based on these considerations, it was decided to test the compatibility of $NaC_{10}$ and of one of the more elaborate carboxylatation solutions with PEG. Nonetheless, since sodium decanoate is known not to protect corroded metal, it was only tested on bare samples. The carboxylatation solution was tested on both bare and corroded material.

The preparation of the sodium decanoate solution consisted in making first a 0.05M sodium hydroxide solution (NaOH) in deionized water, and then adding decanoic acid ($HC_{10}$) in the same proportions (0.05M). This solution was suggested by Hollner since this low concentration works as well as higher ones[566]. The pH of this solution was 7.2 and when added to a 20%v/v PEG 400 solution it became 7.3.

For the carboxylation solution, the oxidant used was hydrogen peroxide ($H_2O_2$) and the acid was decanoic acid. The solution was a mixture of 30g/l of acid, 50% v/v $H_2O$, 50% v/v ethanol, and 0.1M $H_2O_2$[567]. The acid was mixed to the solvents prior to the oxidant to dissolve it more readily. The solution was also heated at 50°C to accelerate its homogenization[568]. The pH of the solution was 3.6. When 20%v/v PEG 400 was added to the solvents, the pH became 3.9. The MSDS of each component of these mixtures are available in appendix 5.

For these two solutions as for the previous one, in the results part, "$NaC_{10}$" means "0.05M $NaC_{10}$" while "carboxylatation solution" is the mixture described above.

[564] Hollner *et al.*, 2007b, p.66.

[565] *Ibid.*

[566] Hollner, oral communication, October 2007.

[567] *Ibid.*

[568] Suggested from Hollner, wrtten communication, March 2008.

## *7.3. Experimental procedure*

### 7.3.1. Set up overview

As discussed in the introduction, impregnation of iron/wood composites was simulated on metal samples to assess the corrosion inhibitors' effectiveness on steel in PEG solution. Accelerated aging was additionally applied. These procedures are well established to test corrosion inhibitors' performances[569].

In regard to treatment simulations on coupons, two different ways of applying the corrosion inhibitors were tested. Either a one-step corrosion inhibitor/PEG mixture was applied by immersion, or a two-step treatment involving immersion in a corrosion inhibitor followed by a PEG bath was used. The idea of a two-step treatment is to protect the metal/wood interface by saturating it with the corrosion inhibitor first, prior to a PEG impregnation. Figure 28 presents the organization of the trials.

This diagram also shows that many samples are tested for each trial to insure reproducibility of results. For bare metal, Degrigny advised repeating each experiment three times[570]. For the already corroded samples, each experiment was replicated five times[571]. This has the drawback of multiplying the number of samples and hence the time taken for the whole experiment, but it insures reliable results. A total of one hundred and forty one samples were thus tested. A number had to be assigned to each sample (fig.28).

The same diagram also shows the reference samples immersed in each "pure" solution (PEG, Hostacor IT®, $NaNO_2$, carboxylatation and $NaC_{10}$) to allow for later comparisons. These are called "reference coupons".

Note that the diagram presents the samples immersed in common baths for ease of illustration. However in practice each coupon was immersed in unique fresh solution in its own jar[572]. The necessary quantity of 120ml jars was obtained from Fisher Scientific® (fig.29).

Lastly figure 28 also shows that only bare metal samples, not corroded samples, were tested in sodium decanoate solution. This decision was reached in consultation with previous studies about $NaC_{10}$ and is discussed in chap.7.2.

[569] See Guilminot's study (2000) and the following articles: Argyropoulos *et al.,* 1999; Argyropoulos *et al.,* 2000; Bobichon *et al.*, 2000.

[570] Degrigny, oral communication, November 2007.

[571] The corrosion may not be exactly the same on each sample. More than three corroded samples are needed for the reliability of each trial. Degrigny, oral communication, November 2007.

[572] Degrigny, oral communication, December 2007.

Figure 28: Trials organization.

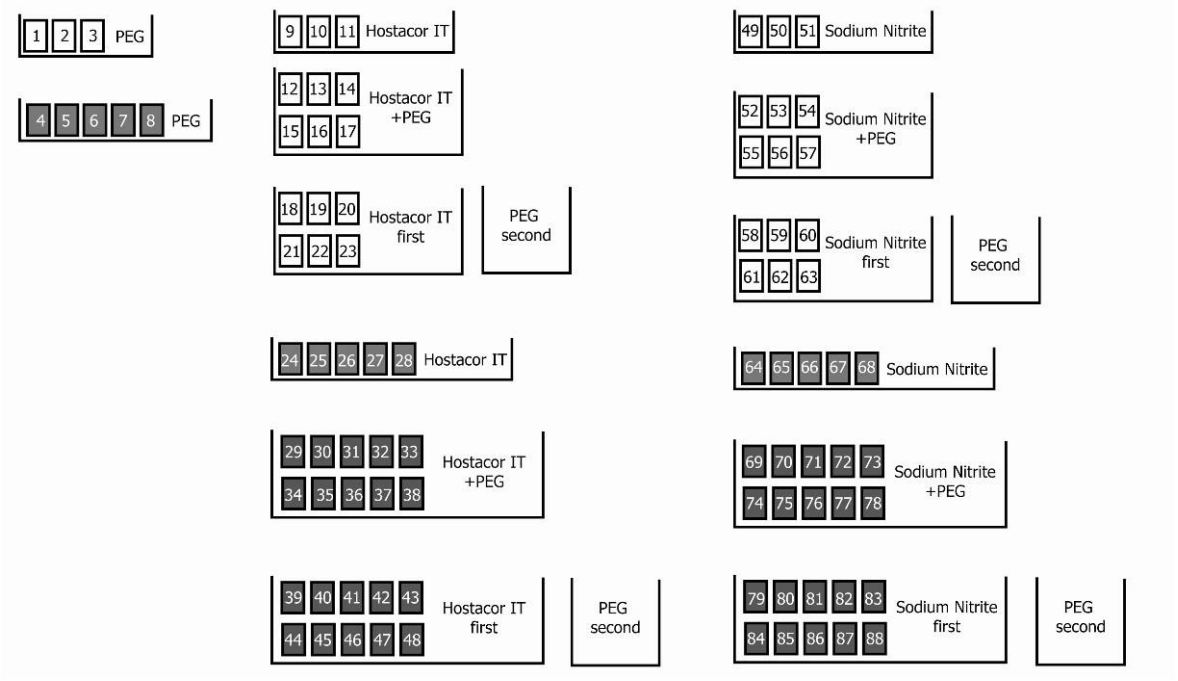

Figure 29: Ecorr monitoring station: one jar equal one sample.

The metal reactivity during treatment was determined for each sample by measuring the corrosion potential (also called $E_{corr}$, Open Circuit Potential -OCP -, Rest or Equilibrium electrode potential[573]).

Effectiveness after treatment was assessed following two accelerated aging methods: half of the one-step treated samples were anodically polarized in concentrated PEG solution (i.e. voltammetry measurements); the other half was placed into a cyclic RH environment generated by an oven.

The following sections discuss these methods.

### 7.3.2. Corrosion potential monitoring versus time

#### 7.3.2.1. DEFINITION OF $E_{CORR}$

*"When a metal gets in contact a* [with a] *conducting solution (electrolyte), the surface reaches a certain energy level, which can be characterized by its potential, measured against a reference electrode"*[574]. The evolution of this potential can be determined by monitoring $E_{corr}$ over time.

Another way to describe $E_{corr}$ is to define it as the sum of all electrochemical half reactions occurring on a metal surface in a solution[575]. As seen in chapter 4, the corrosion of a metal in aerated neutral solution can be described by the following reactions:

- dissolution of metal (oxidation):

(x 4) $M \rightarrow M^{n+} + ne^-$ generating an anodic current, $I_a$ Equation 6

- reduction of dissolved oxygen ($O_{2d}$) in aqueous solution:

(x n) $O_{2d} + 2H_2O + 4e^- \rightarrow 4OH^-$ generating a cathodic current, $I_c$ Equation 7

By adding these two half reactions the equilibrium is ($I_a + I_c = 0$):

$4M + nO_{2d} + 2nH_2O + 4ne^- \rightarrow 4M^{n+} + 4ne^- + 4nOH^-$ Equation 8

or: $4M + nO_{2d} + 2nH_2O \rightarrow 4M^{n+} + 4nOH^- \rightarrow 4M(OH)_n$ Equation 10

$E_{corr}$ corresponds to the situation where $I_a + I_c = 0$.

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[573] Keddam, 1994, p.40; Costa, 2002, p.88; Electrochemistry Dictionary, 2008.

[574] Costa, 2002, p.88.

[575] Degrigny, 2007a.

Therefore, monitoring $E_{corr}$ over time is the only electrochemical measurement that does not disturb the system under study. $E_{corr}$ is influenced by the material and its environment[576].

#### 7.3.2.2. MATERIAL REQUIRED

In addition to the sample (or artifact), the equipment consists of a multimeter, a reference electrode (RE), wires to connect the system together and a timer (fig.30 and 31). The system has to be checked for good electrical contact before beginning the measurements.

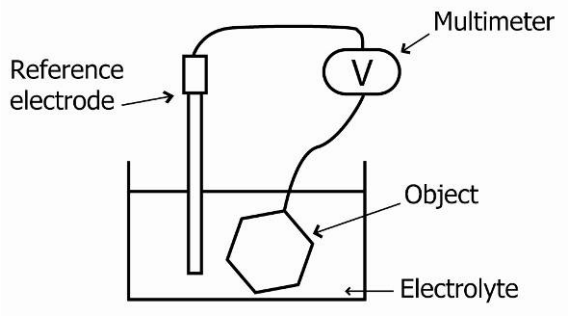


Figure 30: Sketch of Ecorr measurement set up.

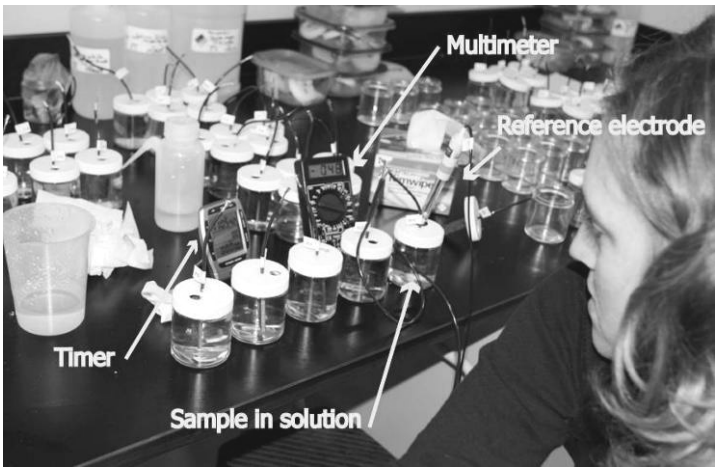


Figure 31: Ecorr monitoring during experiment. Picture: E. Secord, TMM®.

In order to avoid evaporation of the solutions, jars with lids were used. Two holes were drilled through each lid, one for the reference electrode, the other for the wire connected to the sample. When not in use, the holes were covered with Parafilm M® Laboratory Film, in order to avoid evaporation of the solutions and any external pollution.

The $E_{corr}$ monitoring was performed with "silver/silver-chloride" reference electrodes, (Fisher Scientific accumet® Glass Body Ag/AgCl Single Junction High Temperature Reference Electrodes, prefilled with 4M KCl)[577]. They are commonly used REs[578].

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[576] Keddam, 1994, p.40.

[577] Fisher Scientific® catalog number 2008: 13-620-53.

[578] *"The electrode assembly consists of a silver metal electrode in contact with solid silver chloride (usually as a coating on the silver metal) immersed in an aqueous chloride salt solution saturated with silver chloride […] The equilibrium electrode potential is a function of the chloride concentration of the internal electrolyte ("filling solution").*

Five Ag/AgCl electrodes were acquired by the museum in order to devote each probe to a specific solution (PEG, Hostacor IT®, sodium nitrite, carboxylation solution and sodium decanoate). Having several probes avoids contamination of the solutions[579].

The electrodes' potentials were not given in the ER description sheet obtained from Fisher Scientific®. They were verified in tap water with a Metrohm® Ag/AgCl electrode with a known potential of 208,6mV/SHE. This type of measurement cannot be done in deionized water since it is a poor electrolyte. The results versus SHE were the following: electrode A: 204,1mV; electrode B: 203,3mV; electrode C: 200,1mV; electrode D: 193,1mV; electrode E: 203,6mV.

The multimeters used for the experiment were the "Compact Multimeters" from Fisher Scientific®[580].

#### 7.3.2.3. INTERPRETATION OF $E_{CORR}$ OVER TIME RESULTS

Corrosion and passivation states can be clearly determined by examining $E_{corr}$/time graphs. This has been discussed in chapter 4.4.1.2. If the potential increases, there is passivation, if it decreases, there is corrosion[581]. Monitoring $E_{corr}$ on archaeological material, i.e. in presence of corrosion layers, gives different results than on bare metal. If the environment is passivating, the action of a solution on a corroded sample may have a time delay to be effective. The thicker the corrosion layer, the longer it takes to the solution to pass through and passivate the surface[582].

Two months were needed to complete all corrosion potential monitoring planned for this study.

Monitoring $E_{corr}$ over time does not give an indication of the corrosion or passivation rate[583]. This is why such a study is usually complemented by other electrochemical techniques like voltammetry or impedancemetry in corrosion studies[584].

### 7.3.3. Voltammetry

Voltammetry is used *"for the determination of the kinetics and mechanism of electrode reactions, and for corrosion studies. Voltammetry is a family of techniques with the common characteristics that the potential of the working electrode* (metal coupon here) *is controlled (typically with a potentiostat) and the current flowing through the electrode is measured"*[585].

*The most commonly used electrolyte is 4M potassium chloride, producing a potential of 0.222 volt against the standard hydrogen electrode at 25oC (77oF)"* (Electrochemistry Dictionary, 2008).

[579] Degrigny, oral communication, December 2007.

[580] Fisher Scientific® catalog number 2008: S47778, Vendor No.: M-1000C, input impedance of 1 Mega Ohm.

[581] Degrigny, 2007a.

[582] Degrigny, 2004, p.260.

[583] Keddam, 1994, p.40.

[584] *Ibid.*

[585] Electrochemistry Dictionary, 2008. Synonyms of Voltammetry are potentiodynamic polarization, or potential sweep technique (same reference).

On the polarization curves obtained, such as figure 32, i=f(E), "reduction or oxidation reactions are easily identified by negative and positive waves of current occurring at specific potentials in a given electrolyte" [586]. Polarizing a sample under or above the corrosion potential simulates the electrochemical half reactions of corrosion (reduction and oxidation). Reduction reactions occur when the potentiostat scans at values lower than $E_{corr}$, while anodic reactions occur when it is scanning values higher than $E_{corr}$[587].

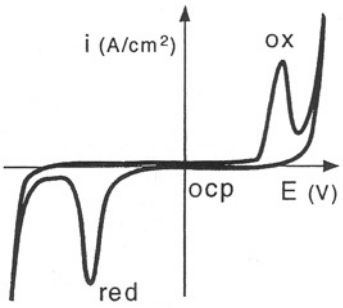


Figure 32: Polarization curve.
From Costa, 2002, p.89.

Measuring both negative and positive polarizations requires testing two identical samples from $E_{corr}$ to cathodic and anodic potentials[588].

The apparatus needed for voltammetry, a potentiostat, is a sophisticated current generator with three channels, controlled by a computer. The three electrodes used are: the working electrode (sample or artifact), the counter electrode (an electrochemically inactive material like platinum or graphite) and the reference electrode[589]. The potentiostat used for the experiment was an EG&G Princeton Applied Research, Model 273A (fig.33). The three electrodes were the following: an Ag/AgCl reference electrode, a graphite counter electrode and a coupon as working electrode. The apparatus was located in the Physics Department of Old Dominion University (ODU) of Norfolk (VA), and is under the responsibility of Dr. D.C. Cook.

The system used the SoftCORR II™ software[590], on a DOS operating system. The data was automatically saved in ".txt" files and had to be manipulated in Microsoft® Excel at ODU before being imported in a European Microsoft® Excel due to compatibility issues[591].


Figure 33: Potentiostat installation at ODU.

Before studying the electrochemical behavior of metal samples in solutions, the electrochemical stability of the solutions should be independently measured[592]. To this end, the potentiostat was first employed to assess the electrochemical activity of

[586] Costa, 2002, p.89

[587] Degrigny, 2004, p.266.

[588] Degrigny, 2007a.

[589] *Ibid.*

[590] Software from the firm Princeton Applied Research.

[591] American ".txt" files are not compatible with European versions of Microsoft® Excel.

[592] Degrigny, 2007a.

the solutions used. This was performed by using a second graphite electrode instead of the working electrode[593]. Thereby, two graphite electrodes were immersed in each solution with the reference electrode (and without metallic sample). The scanning rate was 1mV/s and the range of potentials studied was from -1.6 to 1.6V. The results are presented in the third part of this study (chap.8).

Using this technique on metal samples after treatment can simulate the long term effectiveness of each inhibitor: after PEG/inhibitor treatment of a composite, the metal remains in contact with highly concentrated PEG even after drying. In order to simulate the metal reaction to very concentrated PEG, some samples were polarized in a concentrated PEG 400 solution to stimulate corrosion. For this work, anodic polarizations only were measured to reproduce oxidation to avoid sample duplication and to keep the procedure simple. The results indicate which samples oxidized more readily than other and thereby which inhibitor is more protective in the long term.

The breakdown of the test trials is given in appendix 4. Due to the apparent poor inhibition of the two-step treated coupons (see results chapters) only the one-step treated samples were further analyzed with the potentiostat. For one third of these samples, $E_{corr}$ was monitored previous to polarization. For the other two thirds, the polarization was performed without previous $E_{corr}$ monitoring (see appendix 4). As mentioned above, in agreement with Degrigny, only anodic polarization was undertaken. The scanning rate was constant at 1mV/s. Also, for one third of the samples, the polarization was applied for each coupon from $E_{corr}$ to 1.6V. For the other two thirds, the range of potentials applied was set from -0.25 up to 1.6V[594] base on the parameters of the potentiostat. One month was required to run these experiments.

All voltammetric curves are plotted either as i=f(E) or log(i)=f(E). Sometimes, both curves provided information and are therefore presented in the results. Sometimes, only one of them was used and was included in the following sections.

### 7.3.4. Accelerated aging in a humidity chamber

The other long term effectiveness assessment of the corrosion inhibitors was performed by aging treated coupons in a humidity chamber. These tests simulated an uncontrolled museum environment. To reproduce the conditions, the aging parameters used for the study are the same as those used in the European PROMET project[595]. The parameters applied here were:

- 16 hours at 90% RH and 35°C
- followed by 8 hours in laboratories conditions: 20–25°C and 50-60% RH.

Thirty cycles are required.

[593] Degrigny, written communication, April 2008.

[594] The value of -0.25V was given by the potentiostat.

[595] Degrigny, oral communication, December 2007; Degrigny *et al.,* 2007, p.34; PROMET, 2008.

At 35°C, 90% RH is obtained by placing one centimeter of 4.2M glycerol solution at the bottom of a sealed polyethylene box that contained the samples (according to ASTM standard D5032-97)[596]. The boxes containing the glycerol solutions and samples were placed in an oven to control the temperature as necessary (fig.34 and 35). The samples used for this accelerated aging are represented in a sketch in appendix 2. The humidity chamber was used on the one-step samples, not the two steps samples due to apparent poor inhibition of the two steps treatments (see results section).

This part of the experiment took two months. For days when the coupons could not be accessed, they were placed in polyethylene boxes with silica gel to reduce the humidity and hold the aging process. This procedure was occasionally performed by colleagues when the author was performing experiments at ODU.

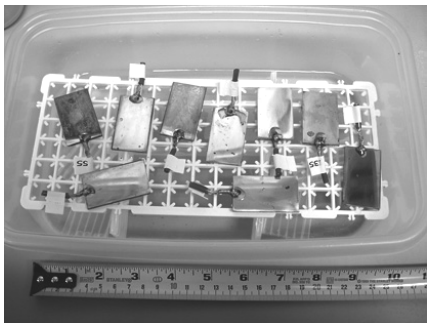


Figure 34: Samples in their polyethylene box, prior to be placed in the oven.

Figure 35: Boxes into the oven.

[596] Degrigny, oral communication, December 2007.

# *Part III: Results and study*

# 8. Electrochemical activity of the solutions

The first objective was to determine whether the solutions used were interfering with the electrochemical reactions occurring on the metal surface, in these solutions. The potentiostat's electrochemical cell was formed of two graphite electrodes that are the working and counter electrodes and the Ag-AgCl reference electrode (see previous chapter). The scanning rate was 1mV/s and the range of potentials observed was from -1.6 to 1.6V. The polarization was performed just after immersion of the graphite electrodes in the solutions.

## *8.1. Electrochemical activity of PEG 400 solutions*

Voltammetric curves were plotted for concentrations of PEG solutions ranging between 20% to 70% (v/v), the two extreme concentrations being used within this project. Figure 36 shows that anodic and cathodic polarizations of graphite, in these solutions, do not present any oxidation or reduction peaks. The small peak observed on this graph (for 20% PEG around -800mV/Ag-AgCl) may be caused by the instrumentation and does not appear to be a meaningful peak[597].

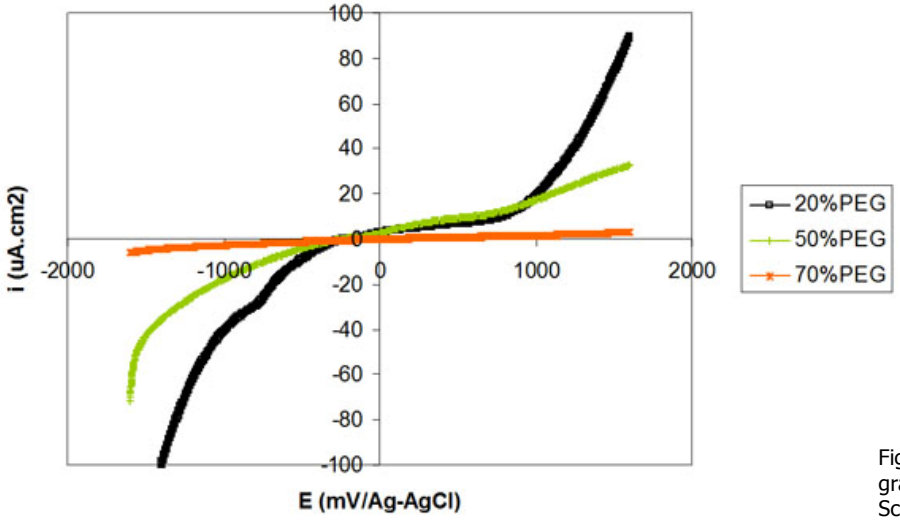



Figure 36: Polarization curves of graphite in different PEG 400 solutions. Scanning rate: 1mV/s.

The anodic current density increases proportionally with the amount of water in solution (maximum at 20%). The oxidation of water occurs around 1V/Ag-AgCl[598]:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$ Equation 24

In the cathodic region, two reactions are involved[599]:

[597] Degrigny, written communication, August 2008.

[598] Guilminot, 2000, p.37; Degrigny, written communication, July 2008.

[599] Guilminot, 2000, p.38; Degrigny, written communication, July 2008.

- reduction of water (starting at -1V/Ag-AgCl): $2H^+ + 2\ e^- \rightarrow H_2$ Equation 9
- reduction of oxygen dissolved (at -0.2V/Ag-AgCl): $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ Equation 25

The only reactions generated by the polarization seen in figure 36 are the decomposition of water. Therefore PEG 400 in the range of concentrations studied can be considered as electrochemically stable[600].

These plots are similar to Guilminot's data although the counter-electrode used in that case was platinum (and not graphite, fig.37 and 38)[601].

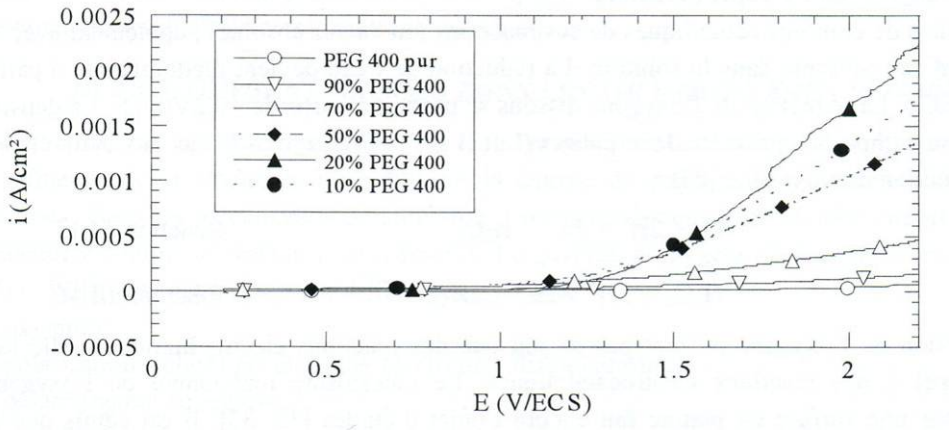



Figure 37: Anodic polarization of platinum at 1mV/s, in PEG 400 solutions. Potentials are versus the Saturated Calomel Electrode (0.242V/SHE). From Guilminot, 2000, p.37.

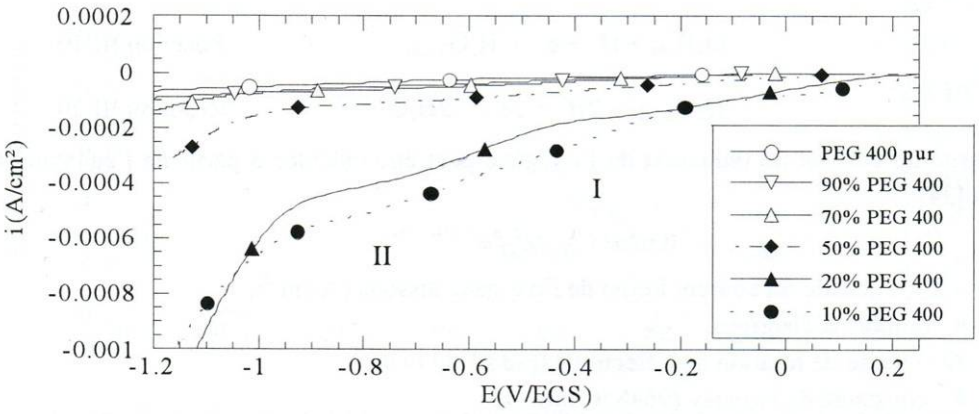



Figure 38: Cathodic polarization of platinum at 1mV/s in PEG 400 solutions. From Guilminot, 2000, p.37.

[600] Degrigny, written communication, July 2008.

[601] Guilminot, 2000, p.37.

## *8.2. Electrochemical activity of the 20% (v/v) PEG 400 / Hostacor IT® solution*

The curves obtained with the mixture 20% (v/v) PEG in deionized water/1% (v/v) Hostacor® are compared to those of 20% (v/v) PEG in water alone and 1% (v/v) Hostacor® in deionized water. All curves are represented in both logi=f(E) and i=f(E) formats in order to better visualize any reaction occurring (fig.39 and 40). The addition of Hostacor® to PEG does not seem to significantly change the corrosion potential of the graphite in Hostacor®. This corrosion potential is slightly lower than for 20% (v/v) PEG alone (fig.39).

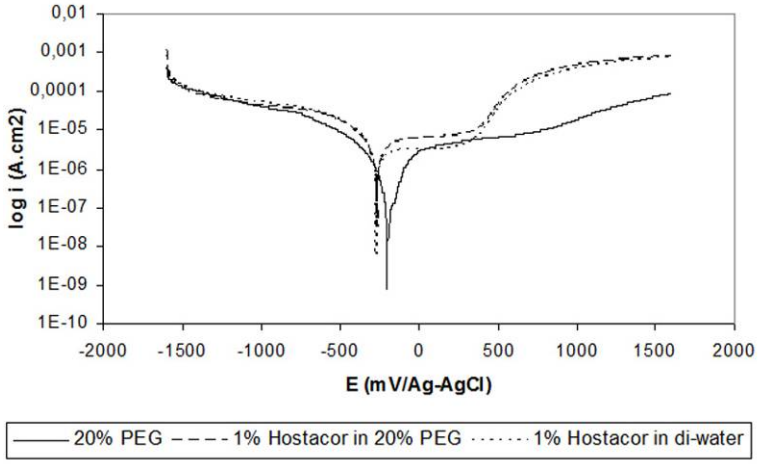



Figure 39: Polarization curves (logi=f(E)) of graphite in 20% PEG 400 solution, 1% Hostacor IT® and 20% PEG 400 + 1% Hostacor IT® solution, scanning rate: 1mV/s.

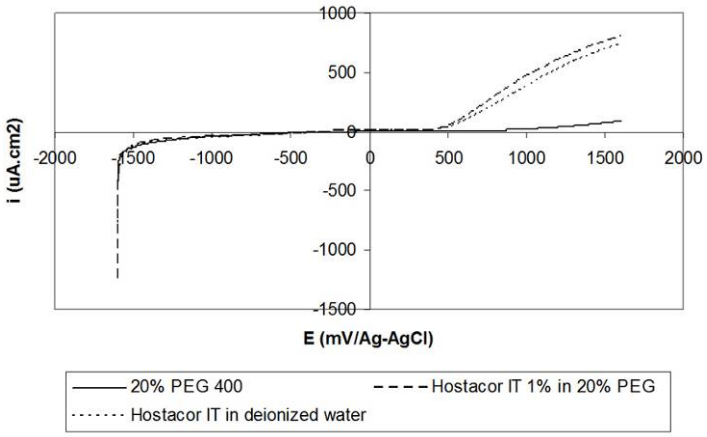



Figure 40: Polarization curves (i=f(E)) of graphite in 20% PEG 400 solution, 1% Hostacor IT® and 20% PEG 400 + 1% Hostacor IT® solution, scanning rate: 1mV/s.

In the anodic region, the oxidation of water in both Hostacor® alone and the PEG/Hostacor® mixture is masked by an oxidation peak around +500mV/Ag-AgCl (figures 39 and 40). According to Guilminot, this increase in current density corresponds to the oxidation of carboxylic compounds in

Hostacor®[602]. No peak appears in the cathodic region, in neither figure 39 nor 40. Guilminot, however, noticed a peak in the cathodic region (-800mV/Ag-AgCl) corresponding to the reduction of the amide functional group[603] (fig.41). This peak seems to be important in 5%v/v solutions of Hostacor® and diminishes significantly in lower concentrations.

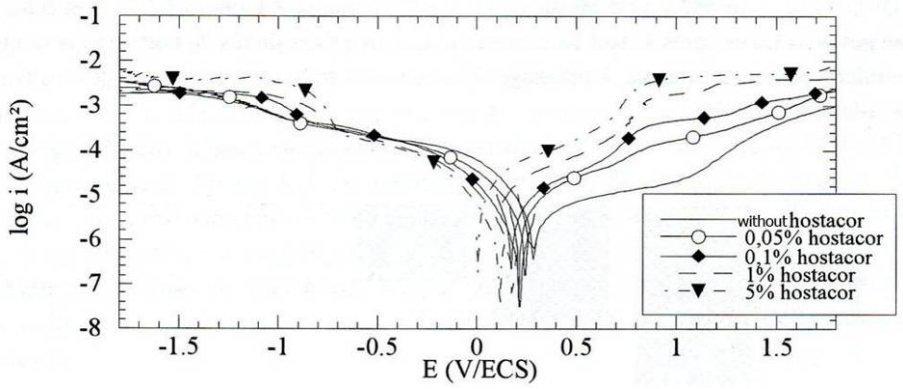



Figure 41: Polarization curves (logi=f(E)) of platinum in Hostacor IT® solutions, scanning rate: 1mV/s. From Guilminot, 2000, p.98.

## *8.3. Electrochemical activity of the 20% (v/v) PEG 400 / $NaNO_2$ solution*

The curves obtained with the 20% (v/v) PEG/100ppm $NaNO_2$ mixture are compared to those of 20% (v/v) PEG alone and 100ppm $NaNO_2$ in deionised water. As with previous data, the results are presented both logi=f(E) and i=f(E) formats (fig.42 and 43). The addition of $NaNO_2$ to PEG increases the corrosion potential of the graphite in comparison to the values in both aqueous $NaNO_2$ and PEG individually.

In the anodic region, the aqueous solution of nitrite shows a peak around 500mV/Ag-AgCl that may corresponds to the oxidation of the nitrite functional group. This peak is still present in the PEG/nitrite mixture but is very small. Interestingly this mixture shows a clear current decrease in the whole anodic region.

No particular features have been observed in the cathodic regions on either the log(i)=f(E) or the i=f(E) graphs.

[602] Guilminot, 2000, p.98.

[603] *Ibid.*

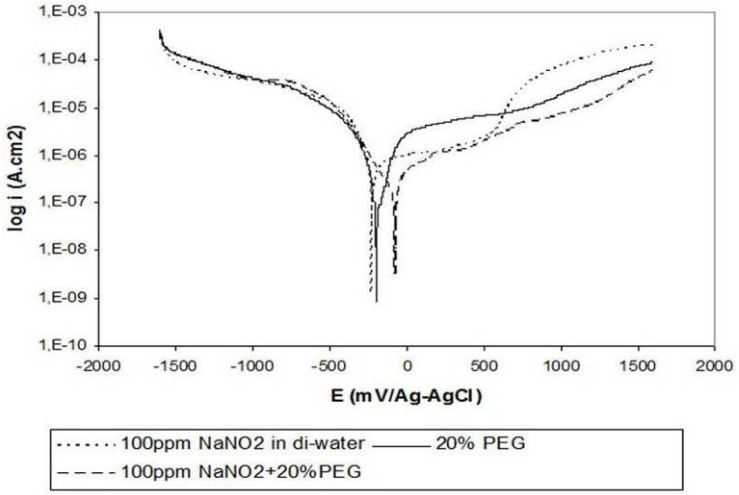



Figure 42: Polarization curves (logi=f(E)) of graphite in 20% (v/v) PEG 400 solution, 100ppm $NaNO_2$, and in 20% PEG 400 + 100ppm $NaNO_2$ solution, scanning rate: 1mV/s.

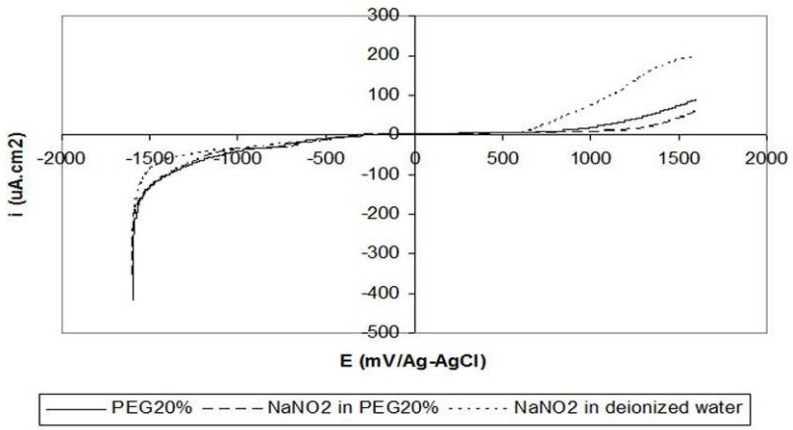



Figure 43: Polarization curves (i=f(E)) of graphite in 20% (v/v) PEG 400 solution, 100ppm $NaNO_2$, and in 20% PEG 400 + 100ppm $NaNO_2$ solution, scanning rate: 1mV/s.

## *8.4. Electrochemical activity of the 20% (v/v) PEG 400 / carboxylatation solution*

The curves obtained with the 20% (v/v) PEG / carboxylatation solution mixture [604] are compared to those of 20% (v/v) PEG and carboxylatation solutions alone. Again data is presented in both logi=f(E) and i=f(E) formats (fig.44 and 45). The carboxylatation solution alone and mixed with PEG similarly increases the corrosion potential of graphite in these solutions compared to PEG alone (figure 44).

[604] As mentioned in section 7.2, carboxylatation solution is a mixture of 50%v/v deionized water, 50% v/v ethanol, 30g/l decanoic acid and 0.1M $H_2O_2$.

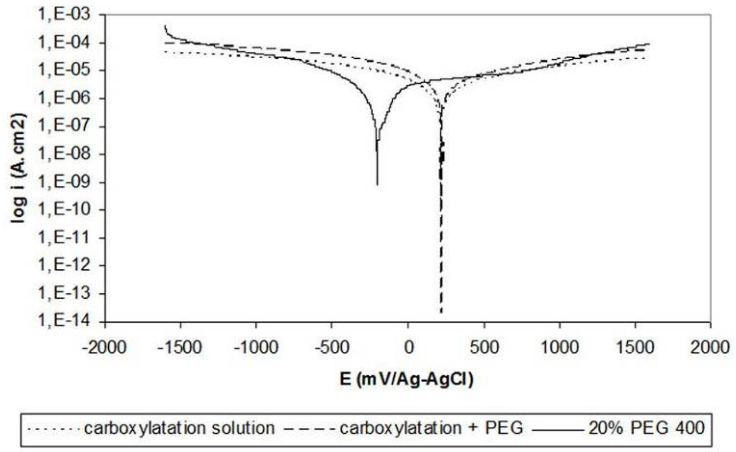



Figure 44: Polarization curves (logi=f(E)) of graphite in 20% PEG 400 solution, carboxylatation solution and 20% PEG 400 + carboxylatation solution, scanning rate: 1mV/s.

Carboxylatation solution alone or mixed with PEG does not create additional anodic or cathodic peaks to the decomposition of water. This is surprising considering the results previously obtained with Hostacor® that showed an anodic peak (around 500mV/Ag-AgCl) corresponding to the oxidation of carboxylic compounds (fig.39). Due to high concentration of carboxylate compounds in this solution, one would expect a similar peak. The cathodic and anodic decomposition of water seem to be shifted as shown more clearly on figure 45.

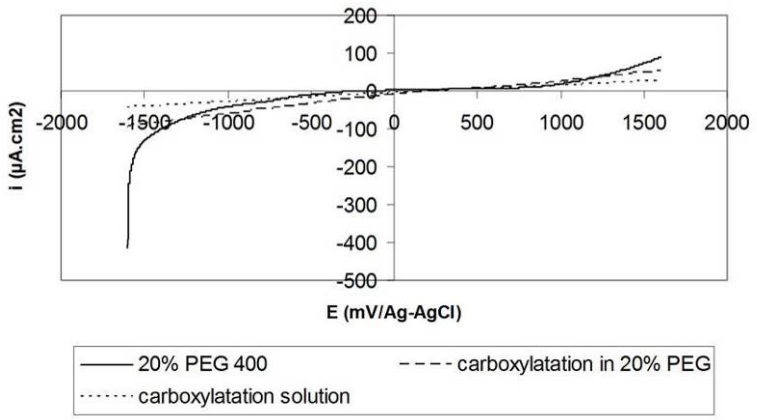



Figure 45: Polarization curves (i=f(E)) of graphite in 20% PEG 400 solution, carboxylatation solution and 20% PEG 400 + carboxylatation solution, scanning rate: 1mV/s

## *8.5. Electrochemical activity of the 20% (v/v) PEG 400 / $NaC_{10}$ solution*

The curves obtained with the 20% (v/v) PEG/0.05M $NaC_{10}$ mixture are compared to those of 20% (v/v) PEG and $NaC_{10}$ solutions alone. Both $NaC_{10}$ solutions decrease the corrosion potential of graphite compared to PEG alone (fig.46). There was even more decrease in corrosion potential in PEG/$NaC_{10}$ mixture.

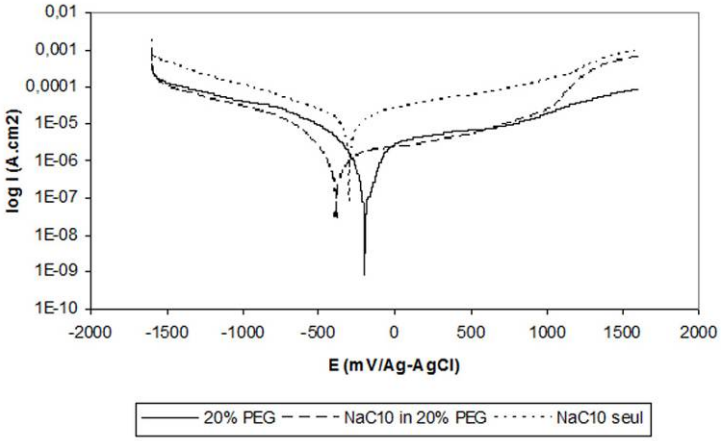



Figure 46: Polarization curves (logi=f(E)) of graphite in 20% PEG 400 solution, 0.05M $NaC_{10}$, and 20% PEG 400 + 0.05M $NaC_{10}$ solution, scanning rate: 1mV/s.

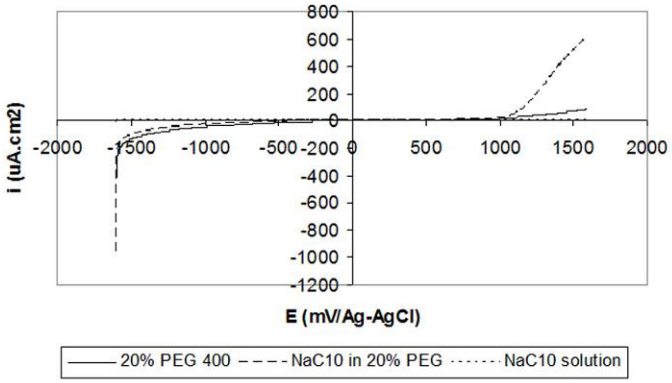



Figure 47: Polarization curves (i=f(E)) of graphite in 20% PEG 400 solution, 0.05M $NaC_{10}$, and 20% PEG 400 + 0.05M $NaC_{10}$ solution, scanning rate: 1mV/s.

$NaC_{10}$ solution alone or mixed with PEG does not seem to create additional anodic or cathodic peaks due to the decomposition of water in oxygen and hydrogen. This is once again surprising considering the results previously obtained with Hostacor® that showed an anodic peak (around 500mV/Ag-AgCl) corresponding to the oxidation of carboxylic compounds (fig.39). The addition of $NaC_{10}$ to PEG seems to favor the oxidation of water as shown by the increase in current around 1000mV/Ag-AgCl. No clear effect of $NaC_{10}$ is observed in the cathodic region.

## *8.6. Conclusions on electrochemical behavior of the solutions*

A solution is called "electrochemically active" when they are anodic and cathodic peaks observed that do not correspond to the decomposition of water[605].

From the data presented above it can be determined that, in the whole range of potential studied:

- 20% (v/v) PEG 400 is electrochemically inactive;

[605] Degrigny, written communication, August 2008.

- 1%(v/v) Hostacor® in deionized water and with PEG is electrochemically active in the anodic region due to the action of carboxylic compounds of Hostacor®;

- sodium nitrite combined with PEG is less electrochemically active in the anodic region than on its own, probably due to the oxidation of the nitrite functional group;

- effects of 0.05M $NaC_{10}$ and carboxylatation solution are unclear. The first tends to favor water oxidation, which is more pronounced in the presence of PEG. The second tends to prevent water decomposition in both anodic and cathodic regions.

Knowing the electrochemical reactivity of the solutions used, it is important now to measure their effect on the samples under study during long immersion periods. For the purpose of this study, samples were immersed for maximum seventeen days.

The behaviors of the samples are first studied in 20% (v/v) PEG solutions. For all solutions, bare samples are examined first and are followed by corroded samples.

Due to practical constraints, the monitoring of $E_{corr}$ was performed for one week

The methodology followed during this study (photos before, during, after treatment and corrosion potential monitoring) is presented thoroughly in the chapter related to immersion in PEG solutions. For other solutions, pictures of the samples are presented in appendices 6 to 9.

For samples treated with PEG solution only (next chapter), the $E_{corr}$ monitoring over time was the sole method used to assess the corrosion behavior of the samples. As discussed in chapter 7, the effectiveness of the inhibitive chemicals was also tested through accelerated aging in a humidity chamber and through voltammetric measurements in concentrated PEG solution (70% (v/v), electrochemically inactive).

# 9. Corrosion behavior of steel samples in 20% (v/v) PEG 400

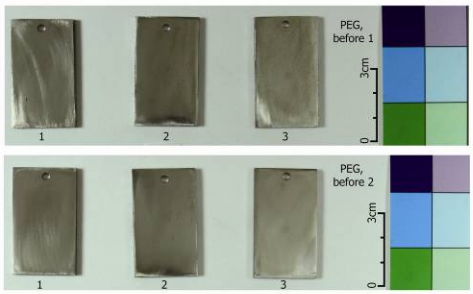
## *9.1. Bare metal*

Figure 48 shows the bare carbon steel samples before, during and after treatment, as well as the corrosion potential monitored over time. The first graph corresponds to the monitoring of $E_{corr}$ over one day, the second one over one week.

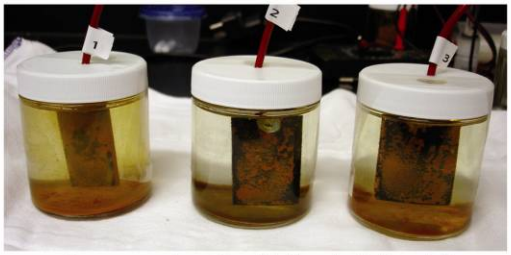
The first graph shows that the potential of the three samples decreased quickly during the first few minutes of immersion. For samples 1 and 2, $E_{corr}$ stopped decreasing after twenty minutes and showed a plateau around -0.7V/Ag-AgCl. For sample 3, this plateau occurred after one and a half hours. The particular behavior of sample 3 showed that although the samples had been identically prepared their surfaces react differently. It reinforces the need to have multiple samples to check the reproducibility of the results. Measurements after three hours showed that the potential remained more or less constant.

Figure 48 shows corrosion of the samples and discoloration of the solution after seventeen days of immersion. The discoloration of the solutions is due to the release of iron ions and was already noticeable after one day of soaking. After two weeks, the corrosion products formed a deposit at the bottom of the jars.

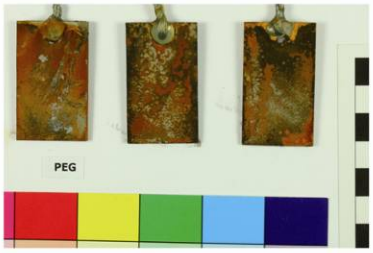
The pH of the solution was between 5.3 and 5.6 and remained stable for seventeen days.



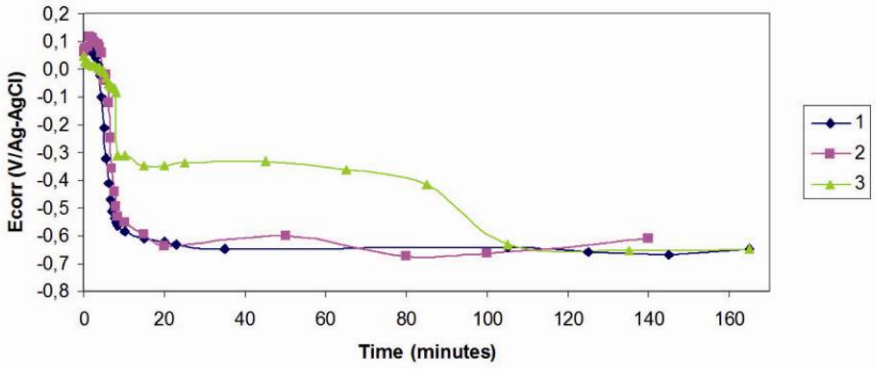

Samples before immersion in PEG



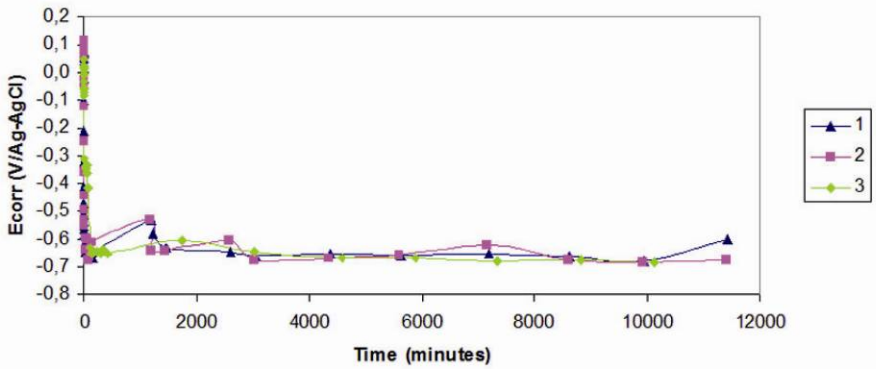
Same samples after 17 days in PEG solution




One side of the samples after 17 days in PEG solution




Ecorr over one day for bare carbon steel in 20% v/v PEG 400

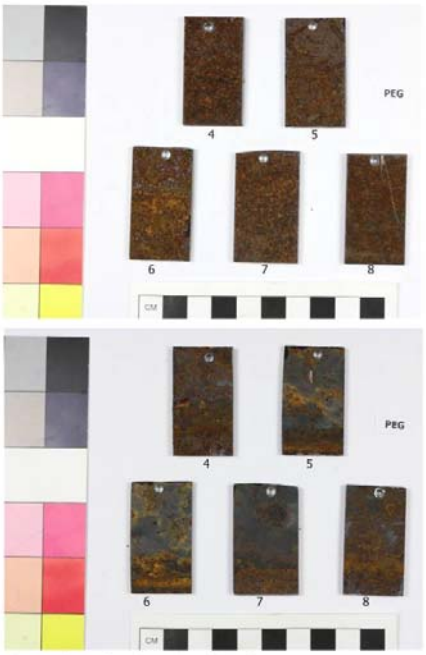



Ecorr over one week for bare carbon steel in 20% v/v PEG 400

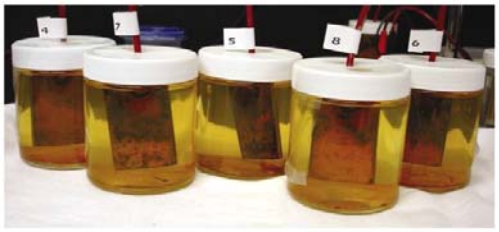
Figure 48: Bare samples before, during and after immersion in 20% (v/v) PEG 400 solution and corrosion potential monitoring versus time of these samples in the solution.

## *9.2. Corroded metal*

The same approach was used on corroded samples. Figure 49 presents the corroded samples before, during and after immersion in 20% (v/v) PEG solution as well as the $E_{corr}$ monitoring over five hours and over one week.

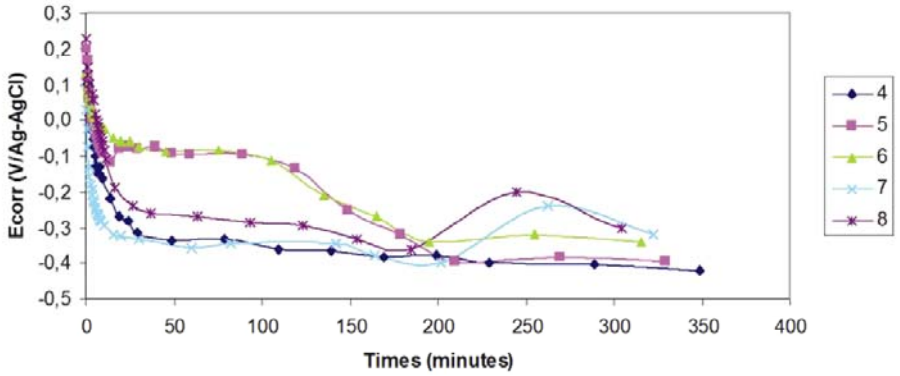



Samples (both sides) before immersion in PEG

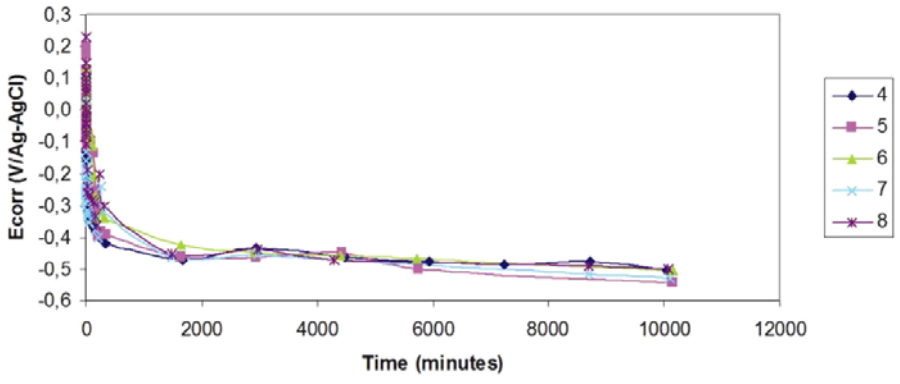


Samples after 17 days of immersion

One side of the samples after 17 days of immersion




Ecorr evolution over one day for corroded samples in PEG




Ecorr evolution over one week for corroded samples in PEG

Figure 49: Corroded samples before, during and after immersion in 20% (v/v) PEG 400 solution and corrosion potential monitoring versus time of these samples in the solution.

As with bare metal coupons, $E_{corr}$ decreased for all corroded samples but at a slower rate. The rates were different for each sample. Some potentials started slightly higher than for bare metal (0.2V/Ag-AgCl versus 0.1V/Ag-Agcl) indicating the passivation effect of the existing corrosion layer on the metal surface. Potentials after four hours were not stable, showing the effect of the corrosion layers on the corrosion behavior of the samples. Depending on the homogeneity of the corrosion layers, the samples reacted differently. Potentials after one day (1440 minutes) decreased and the gap between them narrowed and levelled at -0.5V/Ag-AgCl which is slightly higher than with bare metal samples (-0.7V/Ag-AgCl). This demonstrates the protective effect of the corrosion layers.

Again during immersion corrosion deposits are visible at the bottom of the jars.

According to the pH measurements, the solutions rose from 4 to 5.2 after nine days. It is unknown why the pH of the solution was originally recorded at 4, which is low for a 20% v/v PEG 400 solution. This could be due to more acidic water used for this solution, or due to pH-meter calibration issues.

# 10. Corrosion behavior of steel samples in 20% (v/v) PEG 400 / 1% (v/v) Hostacor IT® mixtures

## *10.1. Electrochemical behavior of carbon steel in 20% (v/v) PEG 400 / 1% (v/v) Hostacor IT®*

### 10.1.1. Bare metal

The following will discuss the behavior of the bare steel samples in:

- 1% (v/v) Hostacor IT® in deionized water (reference solution);
- a mixture of 20% (v/v) PEG400 /1% (v/v) Hostacor IT®, in deionozed water;
- 1% (v/v) Hostacor IT® in deionized water as a pretreatment, followed by an immersion in 20% (v/v) PEG 400.

#### 10.1.1.1. Behavior in 1% (v/v) Hostacor IT® in water

Figure 50 presents the Ecorr values for bare samples in 1% (v/v) Hostacor® solution, over seven hours. Figure 51 corresponds to the same samples over a longer period of one week.

The three bare metal samples showed the same behavior in the 1% (v/v) Hostacor IT® solution: their corrosion potentials increased during the first 6-7 hours indicating a passivation process[606] (fig.50). They remained stable for one week (fig.51) Sample 10 shows a higher potential than the other two, which again shows that even with the same surface treatment, samples can react differently.

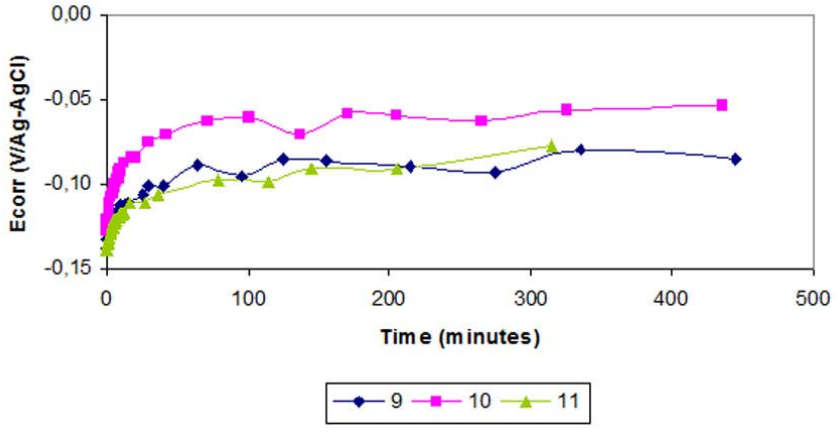



Figure 50: Corrosion potential over time for bare carbon steel samples in 1%(v/v) Hostacor IT® in deionized water.

[606] The variations of $E_{corr}$ occurring around one hundred minutes are due to instrumentation problems. (Degrigny, written communication, March 2008).

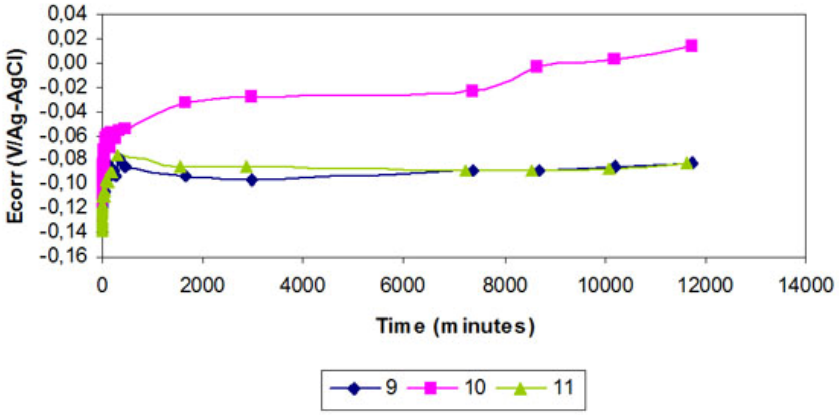



Figure 51: Corrosion potential over time for bare carbon steel samples in 1%(v/v) Hostacor IT® in deionized water.

During sample immersion, the solutions did not discolor and nor was any corrosion products debris observed in the jars (appendix 6). The pH of the solutions were 8.1 and remained stable during two weeks of sample immersion.

#### 10.1.1.2. Behavior in 20% (v/v) PEG 400 / 1% (v/v) Hostacor IT®

Figure 52 presents the $E_{corr}$ values for bare samples in 20% (v/v) PEG 400 / 1% (v/v) Hostacor® solution, over seven hours. Figure 53 corresponds to the same samples over a period of one week. Six bare samples were tested to allow sufficient coupons for different accelerated aging processes.

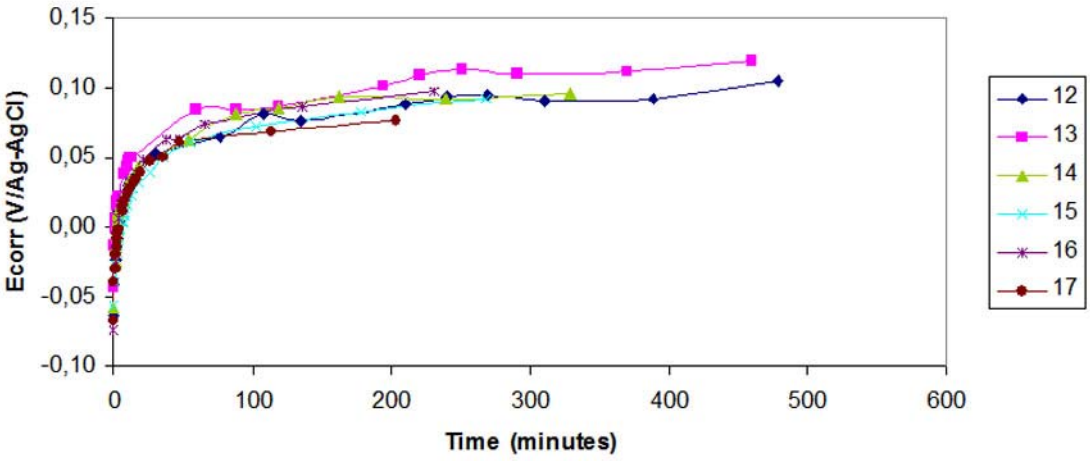



Figure 52: Corrosion potential over time for bare carbon steel samples in 20%(v/v) PEG 400 / 1%(v/v) Hostacor IT® in deionized water.

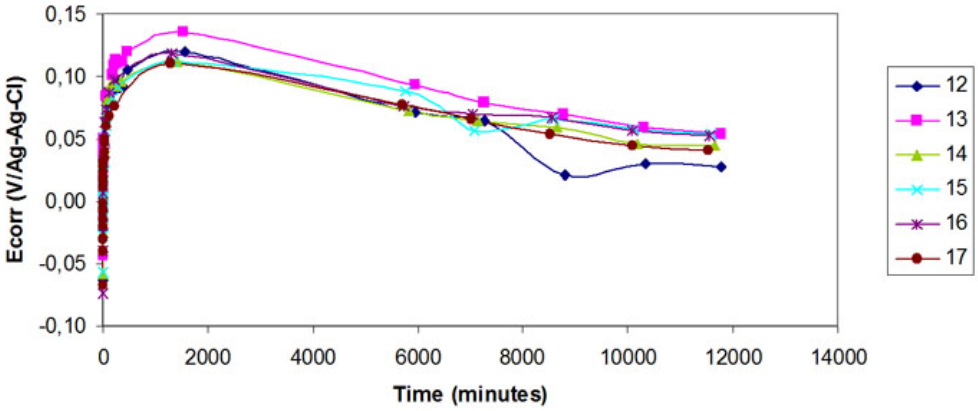



Figure 53: Corrosion potential over time for bare carbon steel samples in 20%(v/v) PEG 400 / 1%(v/v) Hostacor IT® in deionized water.

During the first day of immersion, the metal samples had more or less the same behavior in the PEG/Hostacor IT® solution as in Hostacor® alone. Their corrosion potentials increased versus time indicating a passivation process (fig.52 and 53). This result is comparable to Guilminot's study of iron in this mixture[607]. After one day (fig.53), the corrosion potential diminished steadily. This might be related to the decreased efficiency of Hostacor IT® over time. After two weeks, the solutions did not color and no deposit of corrosion products were observed at the bottom of the jars (appendix 6). The pH of the solutions were 8 and remained stable during the experiment.

#### 10.1.1.3. Behavior in 1% (v/v) Hostacor IT® first, then in 20% (v/v) PEG 400

Figure 54 shows the results for one two-step treated coupon (n°20) as it is representative of all coupons treated with the two-step experiment[608].

During immersion in Hostacor® the metal was passivated (same $E_{corr}$ behavior as in fig.50 and 51). When the same samples were later placed in PEG solution, the $E_{corr}$ decreased readily and stabilized at -0.6V/Ag-AgCl (same behavior as in fig.48, chap.9.2). This shows that the corrosion inhibitor does not form a protective film strong enough to prevent further corrosion in 20% (v/v) PEG solution. If Hostacor® remains at the surface of the samples after immersion the chemical seems to be too diluted in the aqueous PEG. In her PhD, Guilminot demonstrated that when the amount of Hostacor® is too low, the cathodic sites of the metal surface are not protected and become the starting point of corrosion in PEG solution[609].

[607] Guilminot, 2000 , p.104.

[608] As discussed in chapter 7.3 (fig.28), six samples were originally planed for this part of the experiment. However, observing that the first three coupons were not protected by the inhibitor once placed in PEG solution, the other samples were abandoned.

[609] The cathodic sites correspond to impurities of the metal, e.g. manganese sulfurs (Guilminot, 2000, p.126).

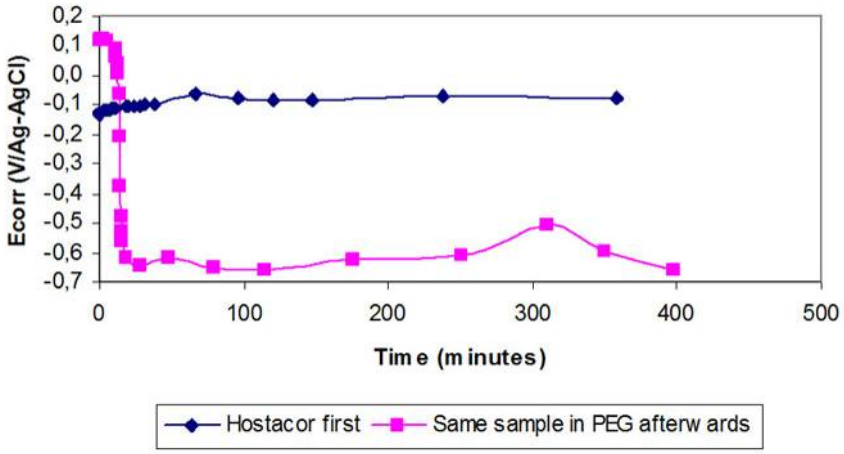



Figure 54: Corrosion potential over time for bare carbon steel samples first immersed in 1%(v/v) Hostacor IT® and then in 20%(v/v) PEG 400.

These results show that Hostacor IT® is an effective inhibitor on its own and in 20% (w/v) PEG solution, on bare carbon steel samples, but not as a treatment prior to 20% (v/v) PEG 400 immersion.

### 10.1.2. Corroded metal

As for bare samples, the following will discussed the behavior of the corroded carbon steel samples in:

- 1% (v/v) Hostacor IT® in deionized water (reference solution);
- a mixture of 20% (v/v) PEG400 /1% Hostacor IT® (v/v), in deionized water;
- 1% Hostacor IT® (v/v) as a pretreatment, followed by an immersion in 20% (v/v) PEG 400.

#### 10.1.2.1. Behavior in 1% (v/v) Hostacor IT® in water

Figure 55 presents the $E_{corr}$ values for corroded samples in Hostacor® solution, over five hours. Figure 56 corresponds to the same measurements over a period of one week.

The initial decreased in $E_{corr}$ occurred sometimes during the first five hours depending on the sample. After the initial decrease the potential gently rose over one week. Such behavior shows the corrosion inhibitor must first penetrate the corrosion layers and is only effective once it has reached the metal surface. Values of $E_{corr}$ after one week were similar to those on bare metal samples (fig.51).

The solution did not change color during immersion, and no corrosion products deposits was observed in the jars. Sample 24 had a slightly different behavior than the others. The higher potentials observed and the quick response of the sample to the solution are certainly related to the presence of less corrosion products at the surface of this particular coupon[610]. The pH of the solutions were 8.1 and remained stable during the experiment.

[610] Degrigny, written communication, March 2008.

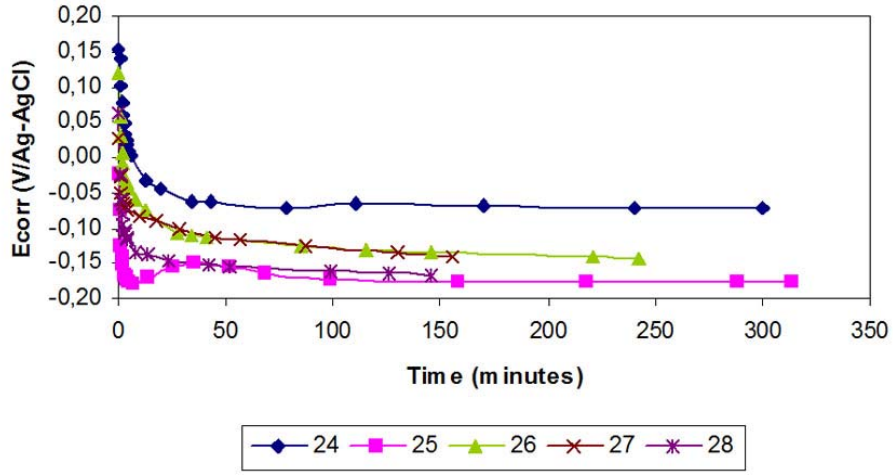



Figure 55: Corrosion potential over time for corroded carbon steel samples in 1%(v/v) Hostacor IT® in deionized water.

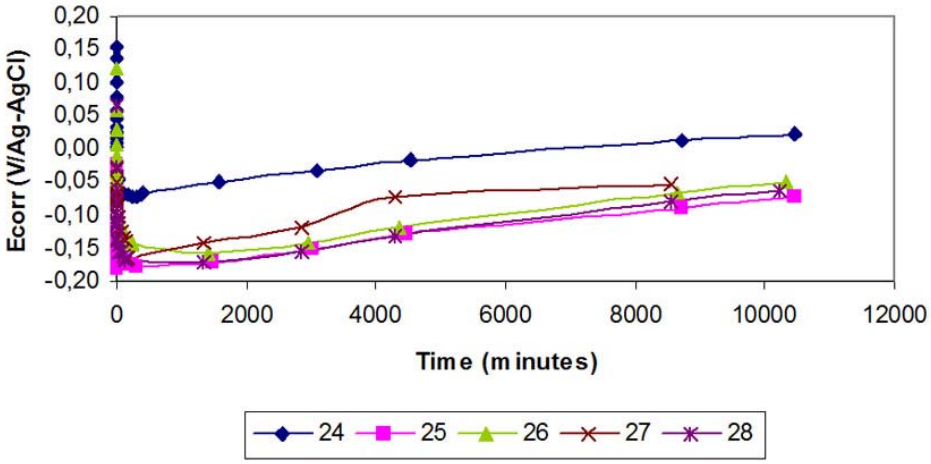



Figure 56: Corrosion potential over time for corroded carbon steel samples in 1%(v/v) Hostacor IT® in deionized water.

#### 10.1.2.2. BEHAVIOR IN 20% (V/V) PEG 400 / 1% (V/V) HOSTACOR IT®

Figure 57 presents the $E_{corr}$ monitoring of corroded samples in 20% (v/v) PEG 400 / 1% (v/v) Hostacor® solution, over seven hours. Figure 58 corresponds to the same measurements over nine days.

$E_{corr}$ initially decreased during the first five to seven hours depending on the sample. After this initial decrease the potential gradually rose for nine days. Again, such behavior shows that the corrosion inhibitor must first penetrate the corrosion layers and is only effective once it has reached the metal surface. Values of $E_{corr}$ after one week are similar to those on bare metal samples. Coupon 34 has a slightly different behavior than the others.

The solutions did not change color after nine days of immersion, and no corrosion product debry was observed in the jars (appendix 6). The pH of the solutions were 8 and remained stable during the experiment.

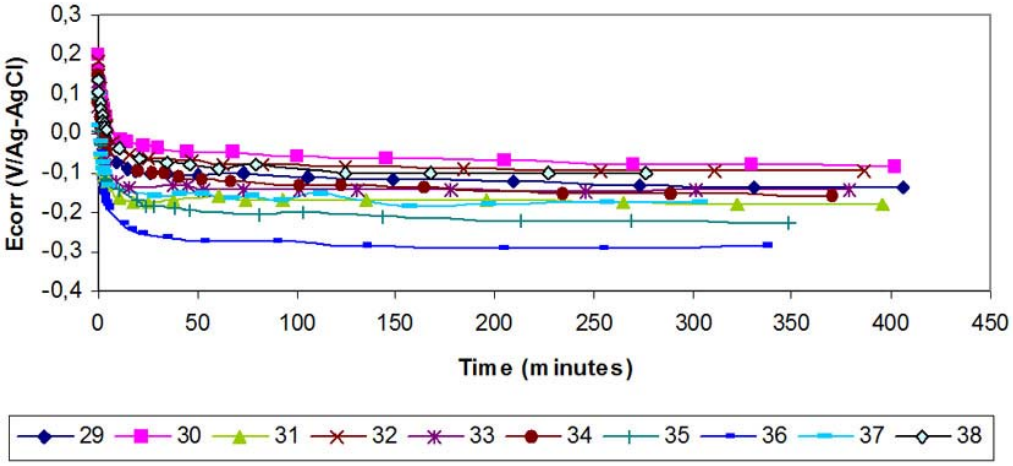



Figure 57: Corrosion potential over time for corroded carbon steel samples in 20%(v/v) PEG 400 / 1%(v/v) Hostacor IT® in deionized water.

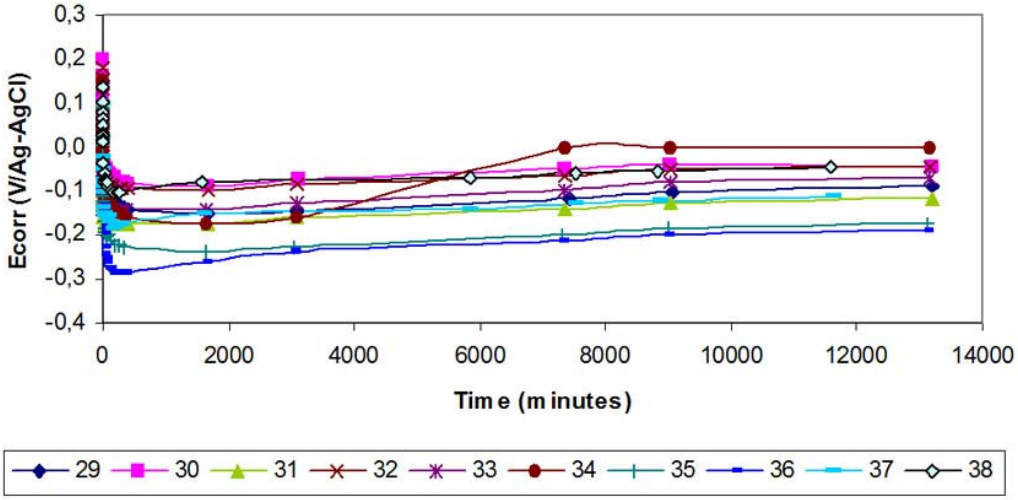



Figure 58: Corrosion potential over time for corroded carbon steel samples in 20%(v/v) PEG 400 / 1%(v/v) Hostacor IT® in deionized water.

#### 10.1.2.3. Behavior in 1% (v/v) Hostacor IT® first, then in 20% (v/v) PEG 400

As for bare samples, figure 59 shows the behavior of one of the five coupons (n°40) tested for this experiment[611]. This coupon is representative of the others and treatment photos of all samples are available in appendix 6.

[611] As discussed in chapter 7.3 (fig.28), six samples were originally planed for this part of the experiment.

The $E_{corr}$ monitoring showed a slight passivation of the coupon, after penetration of Hostacor® solution through the corrosion layers (same behavior as in fig.55). The sample later corroded, in PEG solution, which is also comparable to "corroded samples in PEG solution" (fig.49).

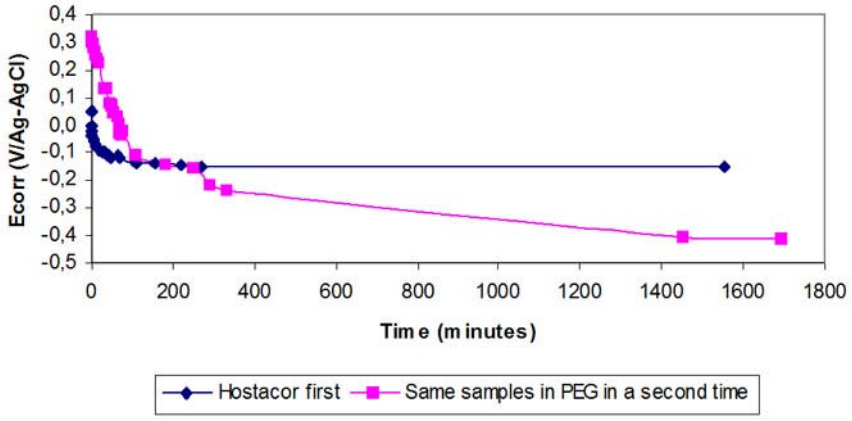



Figure 59: Corrosion potential over time for corroded carbon steel samples immersed in 1%v/v Hostacor IT® first and in 20%v/v PEG 400 afterwards.

Also, as observed for bare carbon steel, immersion in Hostacor® does not prevent the metal from further corrosion when immersed in PEG. The jars also contained debris from corrosion products at their bottom. Also, the treatment photos show a bright rusty color on the surface of the samples due to corrosion (appendix 6).

### 10.1.3. Comparison of results

The following graphs (fig.60 and 61) summarize the results. It is clear that 1% (v/v) Hostacor IT® passivates the surfaces of both bare and corroded carbon steel in 20% (v/v) PEG solution. On bare metal the passivation phenomenon does not seem to last more than a few days. On corroded surfaces, the corrosion inhibitor must first penetrate corrosion products to be effective, yet its efficiency is longer lasting than on bare metal samples.

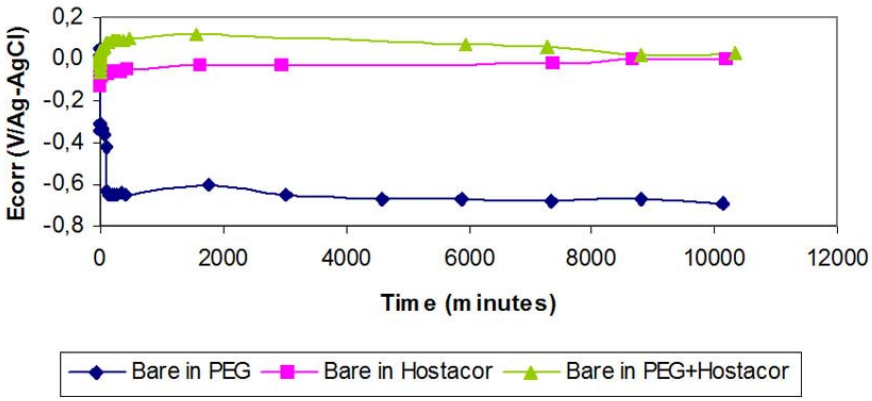



Figure 60: Comparative curves of bare carbon steel in 20% (v/v) PEG 400, 1% (v/v) Hostacor IT® and 20% (v/v) PEG 400 + 1% (v/v) Hostacor IT® solutions.

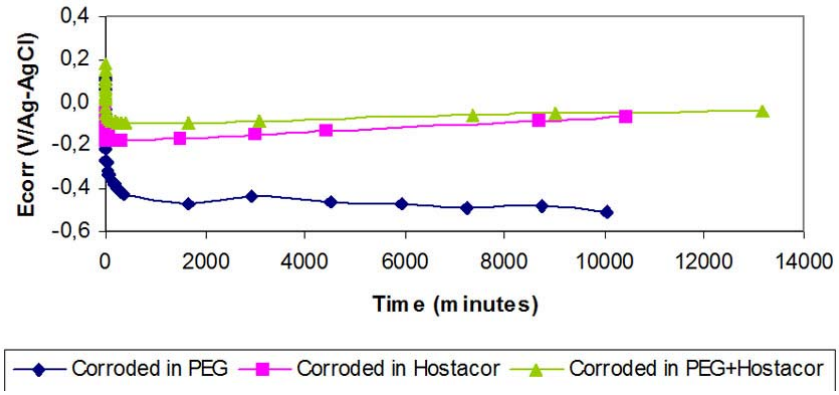



Figure 61: Comparative curves of corroded carbon steel in 20% (v/v) PEG 400, 1% (v/v) Hostacor IT® and 20% (v/v) PEG 400 + 1% (v/v) Hostacor IT® solutions.

It is interesting to note that Hostacor IT® added to PEG is more effective than on its own during the first days of immersion (for both bare and corroded samples). Its protective abilities however decrease steadily over time. This reduction of effectiveness may be due to the decomposition of Hostacor IT®. As the inhibitor acts on metal, it becomes used and spent, which certainly leads to less efficiency of the chemical[612].

## *10.2. Accelerated corrosion tests*

### 10.2.1. Voltammetry in concentrated PEG 400 solution: long term effect of PEG on metal after treatment

As mentioned in section 7.3, the aim of this test was to assess the effectiveness of the corrosion inhibitor on the metal in the long term. Performing anodic polarization of treated samples in 70% (v/v) PEG 400 solution speeds up the corrosion of the metal and simulates the long term exposure of a piece of iron embedded in PEG 400 impregnated wood. Only log(i)=f(E) curves are presented here.

#### 10.2.1.1. BARE METAL

For these trials, bare samples 12 to 14 were anodicaly polarized, after their Hostacor® / PEG 400 treatment. For sample 12, $E_{corr}$ was monitored over time in the 70% (v/v) PEG 400 solution, prior to the polarization of the coupon in the 70% (v/v) PEG 400 solution. Samples 13 and 14 were directly polarized in the concentrated PEG. Samples 102 and 141 are references coupons. Neither received any inhibitive pretreatment before being polarized. Sample 102 was polarized directly in 70% (v/v) PEG 400 solution. Sample 141 was placed in highly concentrated PEG and $E_{corr}$ over time was monitored before polarization. Therefore, the anodic polarization of samples 13 and 14 can be compared to sample 102 and sample 12 compared to sample 141.

[612] Degrigny, written communication, August 2008.

For sample 12, $E_{corr}$ over time monitoring in 70% (v/v) PEG 400 clearly showed a corrosion process in two steps (fig.62). The slow decrease during the first hours may be due to the presence of trace corrosion inhibitor that limits the corrosion process. After this initial decrease, the corrosion accelerated.

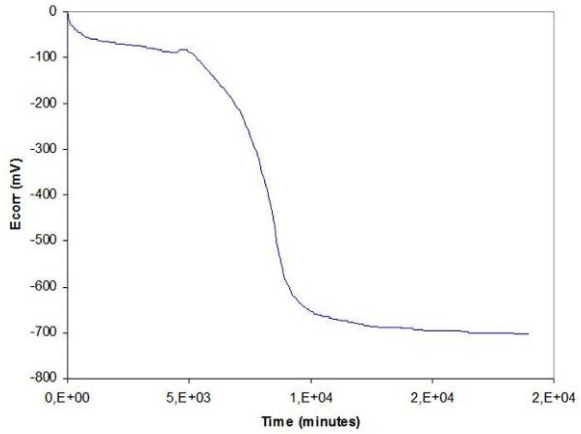



Figure 62: Corrosion potential monitoring of sample 12, in 70% (v/v) PEG 400 solution, after its immersion in 1% (v/v) Hostacor IT® / 20% (v/v) PEG 400 mixture.

The $E_{corr}$ values in the voltammetric plots clearly showed that samples 12 and 141 received a pre-immersion in 70% PEG. Indeed, the $E_{corr}$ for these samples is around -700mV/Ag-AgCl whereas it is around 0mV/Ag-AgCl for samples not pre-immersed in concentrated PEG (fig.63). This pre-immersion step does not seem to have any effect on the shape of the voltammetric curves.

The behavior of sample 13, is rather similar than sample 102. Considering sample 12, the immersion in 70% PEG solution prior to polarization slightly increased the anodic currents. This suggests that this sample could corrode readily. In the case of sample 14 the trace presence of Hostacor IT® might be the cause of the anodic peak around 500mV/Ag-AgCl (see chap.8.2).

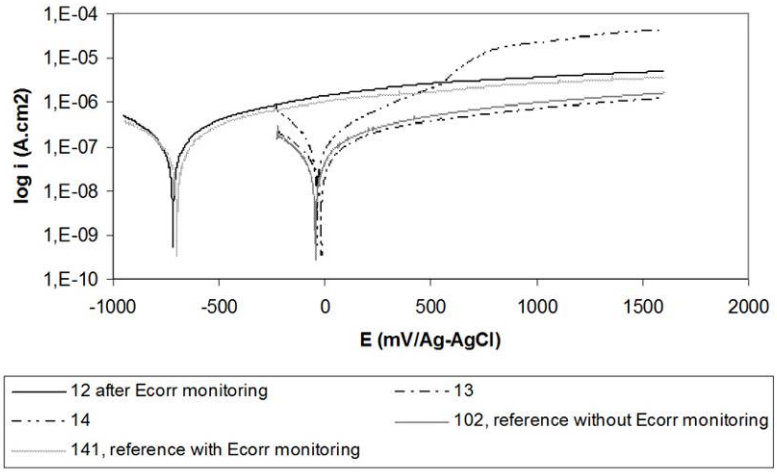



Figure 63: Anodic polarization of bare carbon steel samples in 70% (v/v) PEG 400 solution, after their immersion in 1% (v/v) Hostacor IT® / 20% (v/v) PEG 400 mixture (samples 12 to 14), scanning rate 1mV/s.

#### 10.2.1.2. CORRODED METAL

The same method was applied to five samples of corroded carbon steel to insure the reproducibility of the electrochemical measurements. Samples 29 to 33 were polarized anodically in 70% (v/v) PEG solution, after their pretreatment in the mixture of 1% Hostacor IT®/20% PEG 400. For samples 29 and 30, $E_{corr}$ over time was monitored in 70% PEG solution prior to polarization. Samples 31 to 33 were polarized directly in the solution. Samples 106 and 124 are references coupons and did not pre-treated in the PEG / Hostacor® mixture. Sample 124 was polarized directly in 70% PEG solution and is therefore comparable to samples 31 through 33. The $E_{corr}$ over time of sample 106 was monitored prior to its polarization in 70% PEG solution. Therefore the behavior of samples 29 and 30 are comparable to sample 106.

Figure 64 shows that its corrosion potential of sample 29 decreased steadily over time. However, the corrosion potential did not stabilize.

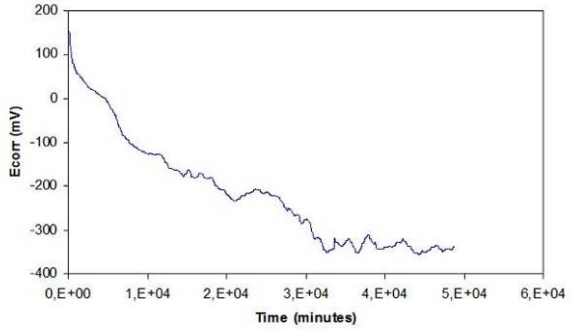



Figure 64: Corrosion potential monitoring of sample 29, in 70% (v/v) PEG 400 solution, after its immersion in 1% (v/v) Hostacor IT® / 20% (v/v) PEG 400 mixture.

With regards to the voltammetric plots, the samples directly polarized (31 and 33) do not behave very differently than the reference sample (124), which was not previously immersed in Hostacor®/20% PEG. It is therefore difficult to confirm that Hostacor® protects the samples in this concentrated PEG solution. Sample 32 showed a slight anodic peak after 500mV/s due to residual Hostacor®. Considering sample 29 (and to a lesser extent sample 106), the immersion in 70% PEG solution prior to polarization increased the anodic currents. This should lead to the ready corrosion of samples.

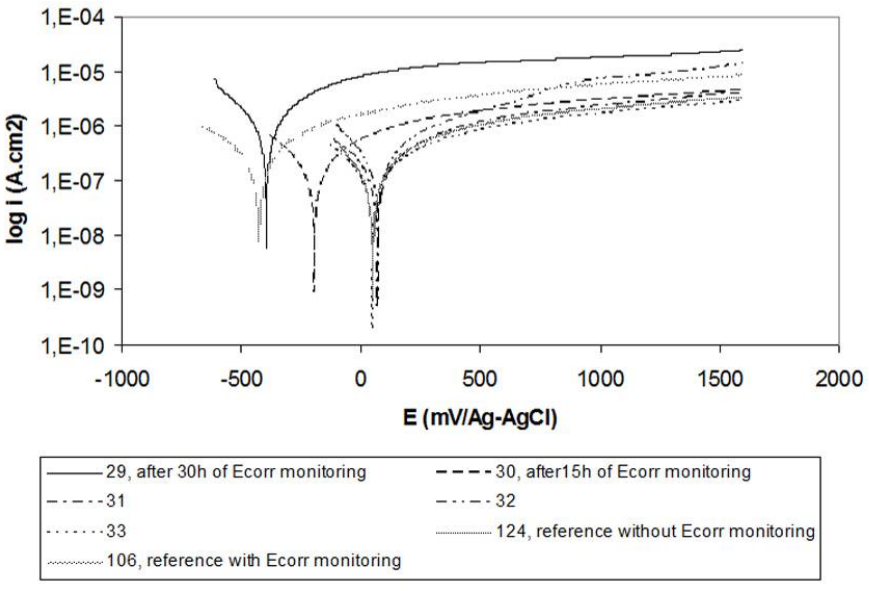



Figure 65: Anodic polarization of corroded carbon steel samples in 70% (v/v) PEG 400 solution, after their immersion in 1% (v/v) Hostacor IT® / 20% (v/v) PEG 400 mixture (samples 29 to 33).

### 10.2.2. Exposure to a humidity chamber

The method used for this test is described in chapter 7.3. The following figures (66 and 67) present the samples before and after treatment with 1% Hostacor/20% PEG 400 mixture followed by the cycles in a humidity chamber.

On bare metal samples, a few black spots of iron oxides developed at the surface of the samples during aging (see fig.66). This could be due to condensation that produces water droplets on the samples when the humidity was at 90% RH. Otherwise, it appeared that the samples remained stable under the imposed environment. This suggests that the corrosion inhibitor continued to protect the metal surface in this simulated uncontrolled environement.

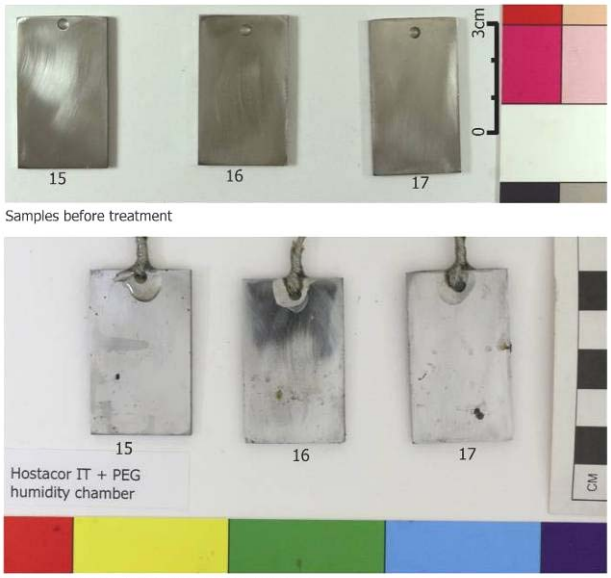



Figure 66: Bare carbon steel samples before treatment and after treatment (immersion in 1% Hostacor® / 20% PEG solution) and aging tests in a humidity chambers over 30 days.

Corroded samples (fig.67) also appeared stable after exposure in the humidity chamber. However, the surface corrosion products became more friable after exposure in the humidity chamber.

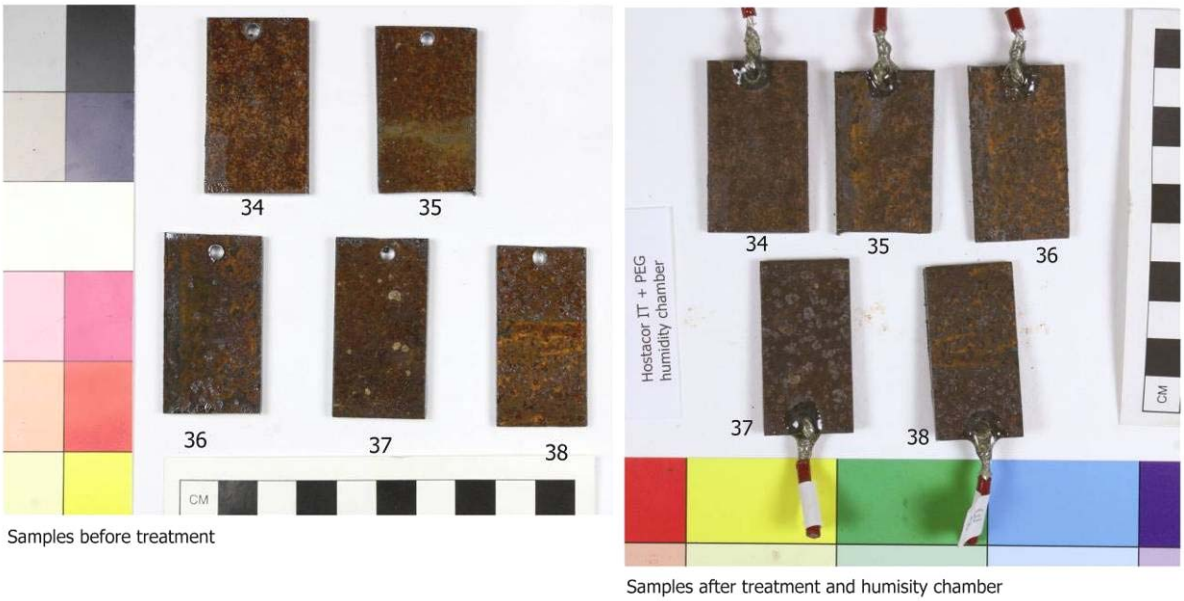



Figure 67: Corroded carbon steel samples before treatment and after treatment (immersion in 1% Hostacor® / 20% PEG solution) and aging tests in a humidity chambers over 30 days.

# 11. Corrosion behavior of steel samples in mixtures 20% (v/v) PEG 400 / 100ppm $NaNO_2$

Similarly to the previous one considering Hostacot IT®. Corrosion potentials monitoring over time is the first method used to assess the effectiveness of sodium nitrite in PEG solution. Accelerated aging are considered in a second time.

## *11.1. Electrochemical behavior of carbon steel in 20% (v/v) PEG 400/ 100ppm $NaNO_2$*

As in the previous chapter, the bare carbon steel samples are discussed first, followed by the corroded one. Each time, the corrosion behavior is observed in 100ppm $NaNO_2$ at first, then in a mixture of 100ppm $NaNO_2$ and 20% (v/v) PEG and finally, in 100ppm $NaNO_2$ followed by 20% (v/v) PEG to simulate a pre-treatment by the corrosion inhibitor followed by an immersion in PEG solution.

### 11.1.1. Bare metal

#### 11.1.1.1. Behavior in 100ppm $NaNO_2$ in water

The three bare metal samples had the same behavior in the 100ppm $NaNO_2$ solution: their corrosion potentials increased over time (at least during the first 6-7 hours) indicating a passivation process (fig.68). The measurements made over one week showed stable $E_{corr}$ values (fig.69). The potentials are slightly higher than for Hostacor® (0.05 instead of -0.05V/Ag-AgCl), indicating a better protection[613].

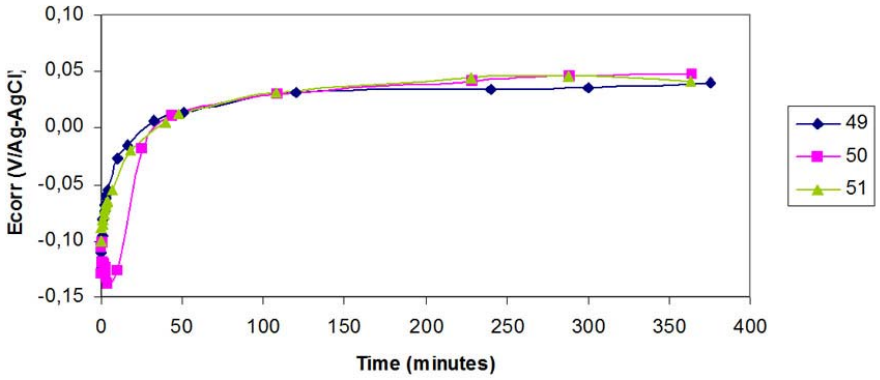



Figure 68: Corrosion potential over time for bare carbon steel samples, during one day, in 100ppm $NaNO_2$ in deionized water.

[613] Degrigny, written communication, March 2008.

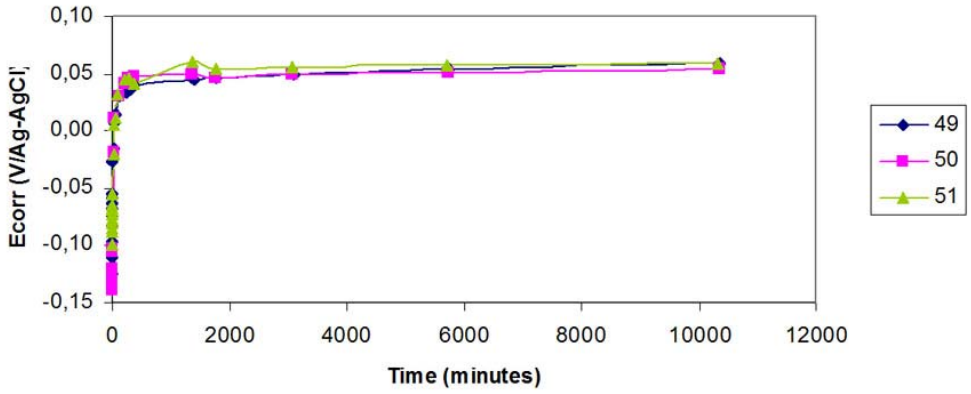



Figure 69: Corrosion potential over time for bare carbon steel samples, during one week, in 100ppm $NaNO_2$ in deionized water.

The solutions did not color and no deposit of corrosion products were observed at the bottom of the jars (appendix 7).

The pH of the solutions was of 6.6 and remained stable during the two weeks of immersion. This pH is rather low for iron based alloys and there is a good chance that if sodium nitrite gets consumed, corrosion will start[614].

#### 11.1.1.2. Behavior in 20% (v/v) PEG 400 / 100ppm $NaNO_2$

The six metal samples had, more or less, all the same behavior in the 20% PEG / 100ppm $NaNO_2$ solution: their corrosion potentials rose over time indicating then a passivation process, at least during three days the measurements (fig.70 and 71). A decrease of the potentials is observed after 6000 minutes for sample 52, 53, 54 and 56. The potentials are higher than for $NaNO_2$ solutions only, indicating a better passivation process.

Most of the solutions did not color and no deposit of corrosion products were observed at the bottom of the jars (appendix 7). Samples 52 and 55 were slightly corroded after ten days in solution and the corresponding solutions turned steadily yellowish. The evolution of the corrosion potential over time of sample 52 confirms this alteration. The degradation of sample 55 is more difficult to understand. The low pH of the solutions (pH of 4.2 that remained stable during the experiment) might have initiated the corrosion of these samples[615].

[614] Degrigny, written communication, March 2008.

[615] As mentioned in chapter 7, the reasons why this pH is so low are still not fully understood and require further study. The very weak concentration of sodium nitrite in these solutions (100ppm, i.e. $1.45.10^{-3}$M) was perhaps too low to protect these two samples.

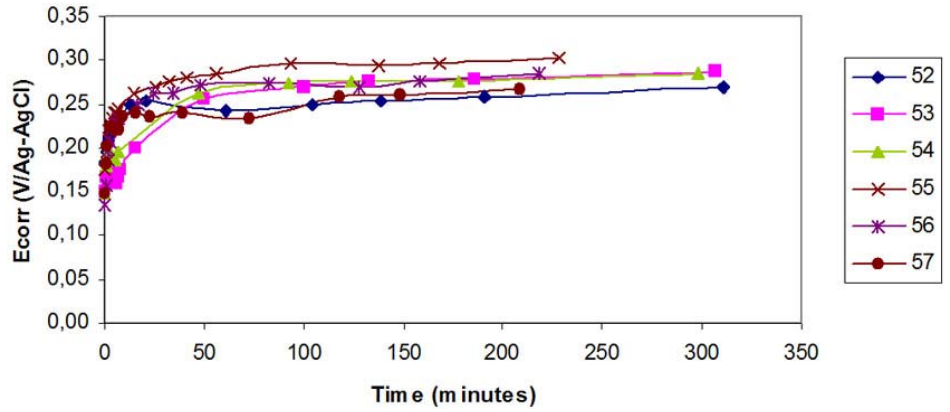



Figure 70: Corrosion potential over time for bare carbon steel samples, over one day, in 20%(v/v) PEG 400 / 100ppm $NaNO_2$ in deionized water.

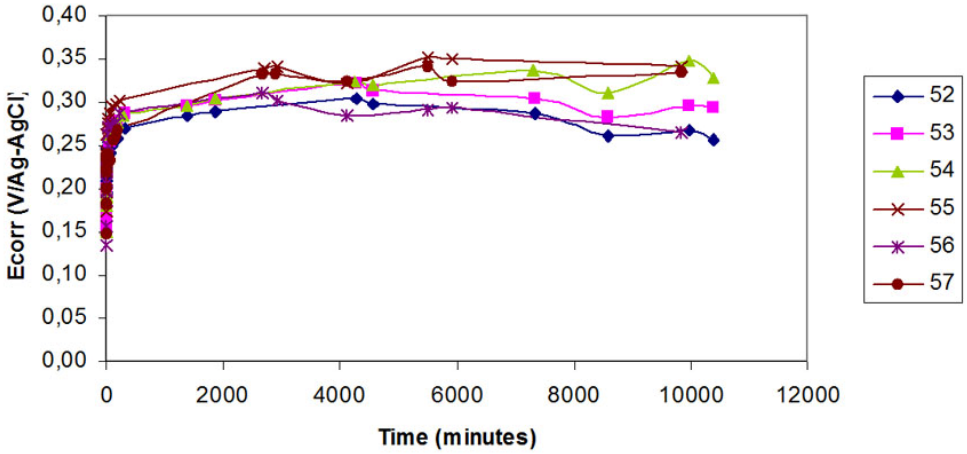



Figure 71: Corrosion potential over time for bare carbon steel samples, over one week, in 20%(v/v) PEG 400 / 100ppm $NaNO_2$ in deionized water.

#### 11.1.1.3. BEHAVIOR IN 100PPM $NaNO_2$ FIRST, THEN IN 20% (V/V) PEG 400

Figure 72 shows that bare samples were first passivated in sodium nitrite solution (corrosion potential increasing) and that they corroded, afterwards, in PEG solution (decreasing of $E_{corr}$). Therefore, as observed with Hostacor IT®, sodium nitrite cannot be used as a pretreatment to PEG to protect the metal.

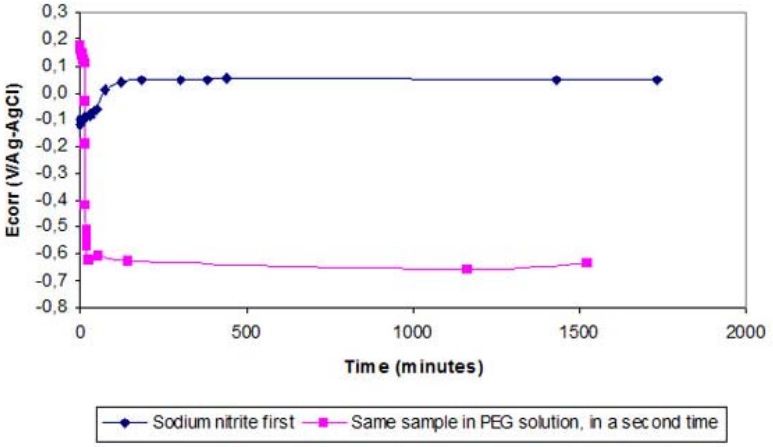



Figure 72: Corrosion potential over time for bare carbon steel samples first immersed in 100ppm $NaNO_2$ and then in 20%(v/v) PEG 400.

### 11.1.2. Corroded metal

#### 11.1.2.1. Behavior in 100ppm $NaNO_2$ in water

As figure 73 shows it, $E_{corr}$ values decreased during the first minutes (much shorter than with Hostacor®, see fig.56). The behavior is rather reproducible for all samples. Only the values are different indicating certainly a difference in the level of corrosion coverage of the metal surface. The re-increase of the corrosion potential occurs quite fast too (after less than one hour) and continues till five days (8000 minutes, see fig.74). Such behavior shows that first the corrosion inhibitor has to penetrate through the corrosion layer and is only effective when it has reached the metal surface. Potentials are also higher than for Hostacor® (between -0.3 and 0V/Ag-AgCl for Hostacor® and -0.1 and 0.1V/Ag-AgCl in this case), indicating a better passivation which is confirmed in the long term.

Values of $E_{corr}$ after one week are slightly higher to those on bare metal samples (see fig.69).

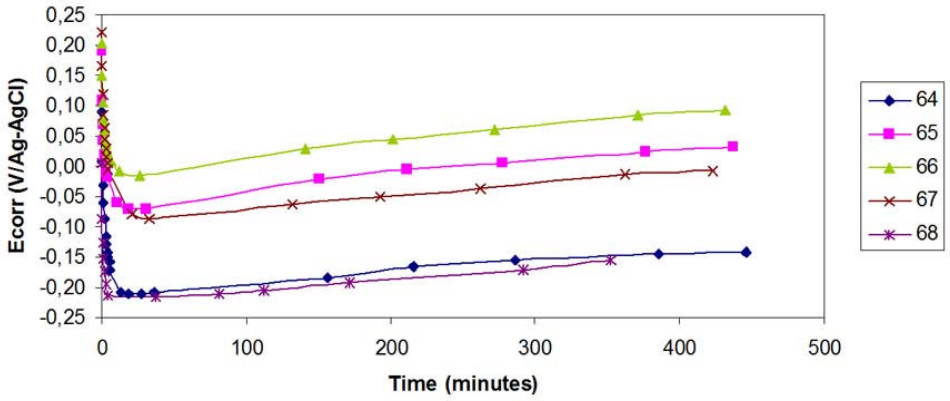



Figure 73: Corrosion potential over time for corroded carbon steel samples in 100ppm $NaNO_2$ in deionized water.

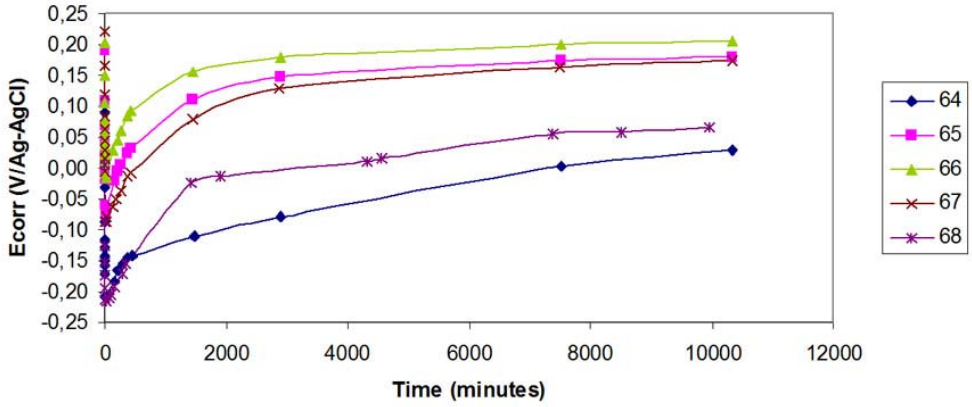



Figure 74: Corrosion potential over time for corroded carbon steel samples in 100ppm $NaNO_2$ in deionized water.

Most of the solutions did not change color after twelve days of immersion and no corrosion products were observed in the jars, except for samples 64 and 68 (see appendix 7). As shown on figures 73 and 74, these samples presented also the lowest potentials which should indicate that their corrosion layers were the thinnest or less covering. Still passivation occurred for these coupons. We may conclude that

in that case the corrosion layers were less adherent to the metal surface and some elements eventually fell down.

The pH of the solutions were 6.6 and remained stable during the experiment.

#### 11.1.2.2. BEHAVIOR IN 20% (V/V) PEG 400 / 100PPM $NaNO_2$ SOLUTION

Figure 75 shows that that $E_{corr}$ decreased during the first minutes to two hours depending on the sample. Beyond (till five days, fig.76), the potential increased. Such behavior shows again that first the corrosion inhibitor has to penetrate through the corrosion layers and is only effective when it has reached the metal surface. Values of $E_{corr}$ after five days are lower to those on bare metal samples (around 0.3V/Ag-AgCl, see fig.72, against -0.1V/Ag-AgCl here).

The solutions became yellowish over time, meaning that iron ions passed in solution (appendix 7). This might corresponds to the time needed by the corrosion inhibitor to reach the metal surface, when the metal is not protected. Indeed, the pH of the solution is low, 4.2, and the following reaction might have occurred[616]: $Fe(OH)_3 + H^+ \rightarrow Fe^{3+} + H_20$ Equation 26

For samples 69, 70, 71, 75 and 76, the pH increased from 4.2 to 5.2 during the experiment. For the others, pH passed from 4.2 to 4.6.

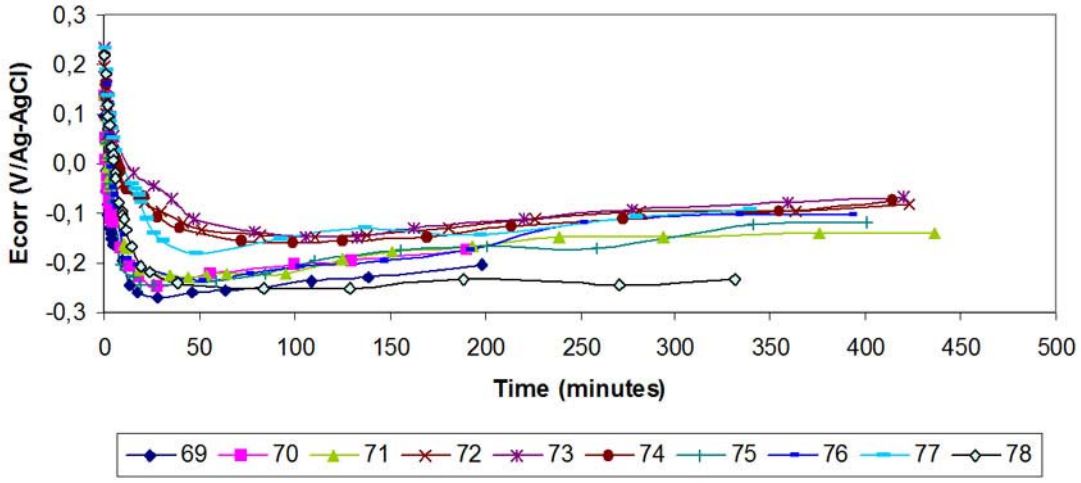



Figure 75: Corrosion potential over time for corroded carbon steel samples in 20% (v/v) PEG 400 / 100ppm $NaNO_2$ in deionized water.

[616] Degrigny, written communication, March 2008.

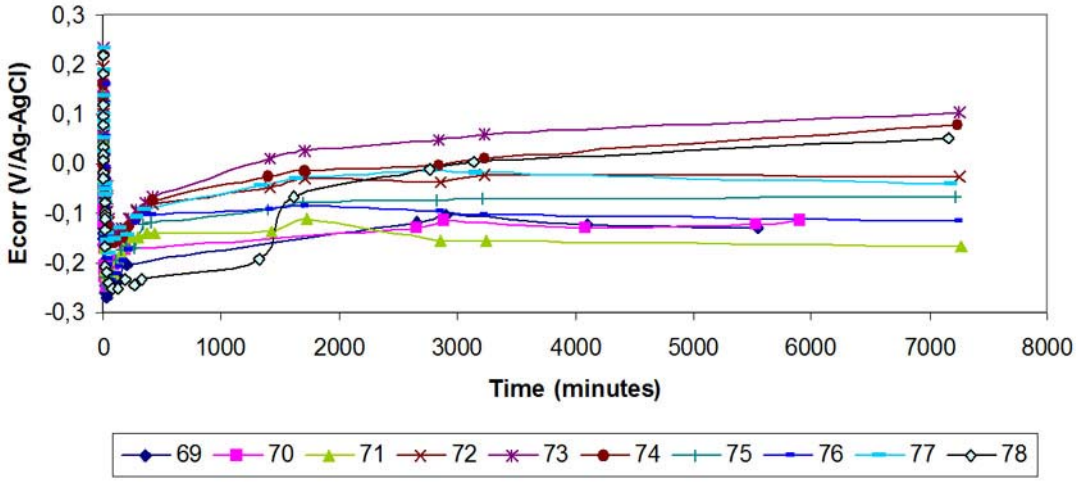



Figure 76: Corrosion potential over time for corroded carbon steel samples in 20% (v/v) PEG 400 / 100ppm $NaNO_2$ in deionized water.

#### 11.1.2.3. BEHAVIOR IN 100PPM $NaNO_2$ FIRST, THEN IN 20% (V/V) PEG 400

Figure 77 shows that the corrosion potential indicated a slight passivation of the samples after penetration of $NaNO_2$ through the corrosion layer (same behavior as before). When placed in PEG solution afterwards, the samples corroded as the decrease of $E_{corr}$ shows it.

As observed on bare samples, these trials showed that a sodium nitrite pre-immersion does not protect the samples enough from corrosion when immersed afterwards in PEG solution.

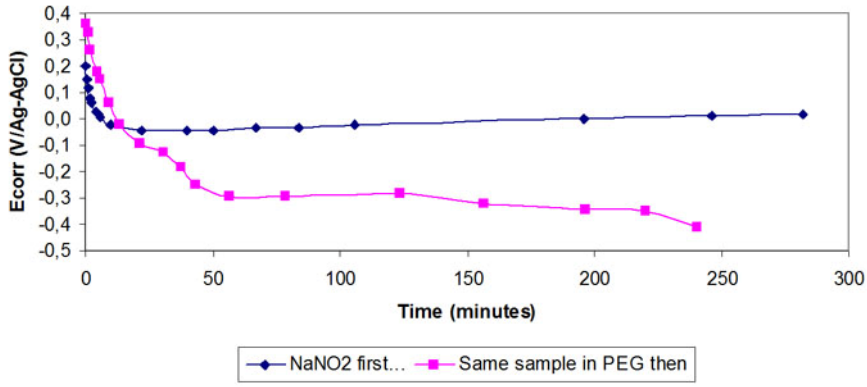



Figure 77: Corrosion potential over time for corroded carbon steel samples first immersed in 100ppm $NaNO_2$ and then in 20%(v/v) PEG 400.

### 11.1.3. Comparison of results

The following graphics (fig.78 and 79) summarize the experiments over five days of immersion for bare and corroded samples. 100ppm $NaNO_2$ solution passivates the surfaces of both bare and corroded carbon steel in 20% (v/v) PEG 400 solution. This passivation is even better than when $NaNO_2$ is used alone on bare metal samples. On corroded surfaces, the corrosion inhibitor has first to penetrate through the corrosion products to be effective.

However, the discoloration of the solutions during the experiment suggests the release of iron ions for two bare samples and for all corroded samples, in $NaNO_2$/PEG solutions. The low pH of the solution might be responsible for these corrosion cases. The chemistry of the solution suggests that sodium nitrite helps the deprotonation of PEG, provoking this low pH. Even though more studies are needed to confirm this statement, this issue might show that sodium nitrite is not compatible with PEG[617].

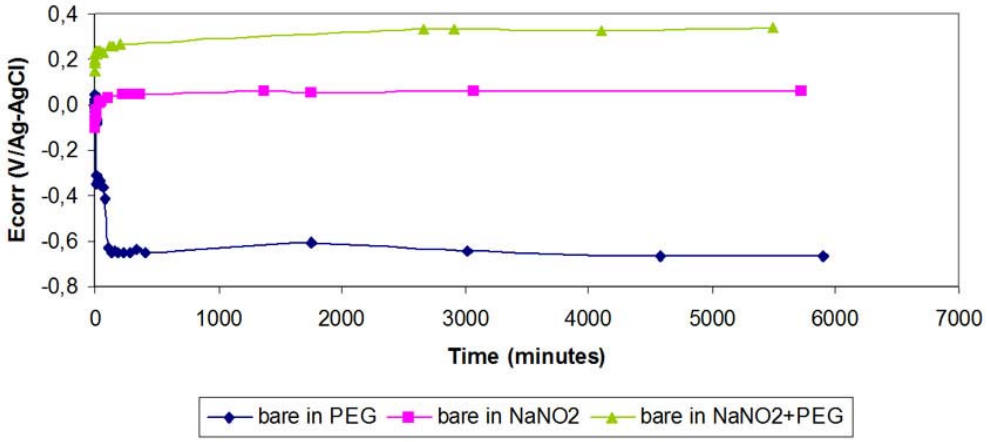



Figure 78: Comparative curves of bare carbon steel in 20% (v/v) PEG 400, 100ppm $NaNO_2$ and 20% (v/v) PEG 400 + 100ppm $NaNO_2$ solutions.

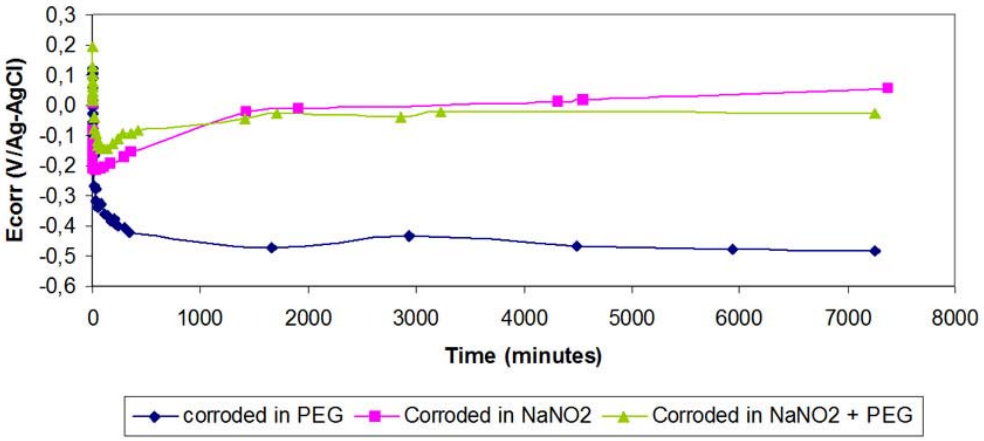



Figure 79: Comparative curves of corroded carbon steel in 20% (v/v) PEG 400, 100ppm $NaNO_2$ and 20% (v/v) PEG 400 + 100ppm $NaNO_2$ solutions.

[617] Domjan, Chemistry Teacher, HEAA-Arc, written communication, August 2008.

## *11.2. Accelerated corrosion tests*

### 11.2.1. Voltammetry in concentrated PEG solution: long term effect of PEG on metal

As mentioned in section 7.3, and 10.2, performing anodic polarization of treated samples in 70%v/v PEG 400 solution should speed up the corrosion of the metal and simulate the long term exposure of a piece of iron embedded in wood impregnated with PEG 400. As in chapter 10, only log(i)=f(E) curves are presented here.

#### 11.2.1.1. BARE METAL

Bare samples 52 to 54 were anodicaly polarized, after their 20% (v/v) PEG 400/100ppm $NaNO_2$ treatment. For sample 52, $E_{corr}$ was monitored over time, in the 70% (v/v) PEG 400 solution, prior to the polarization of the coupon, in the 70% (v/v) PEG 400 solution. Samples 53 and 54 were polarized directly in this solution. As in chapter 10.2, samples 102 and 141 are references coupons. Neither received any inhibitive pretreatment before being polarized. Sample 102 was polarized directly in 70% (v/v) PEG 400 solution. Sample 141 was placed in highly concentrated PEG and $E_{corr}$ over time was monitored before polarization. Therefore, the anodic polarization of samples 53 and 54 should be compared to the one of sample 102 and sample 52 to the one of sample 141.

For sample 52, $E_{corr}$ over time clearly shows, like for Hostacor®, a corrosion process in two steps (fig.80). The slow decrease during the first hours might be due to the presence of traces of the corrosion inhibitor that limits the corrosion. Afterwards the corrosion process speeds up. This coupon corrodes slower than sample 12 tested after an immersion in Hostacor®/ PEG solution (see fig.62). This suggests a better long term protection of $NaNO_2$ than Hostacor IT® on concentrated PEG solution.

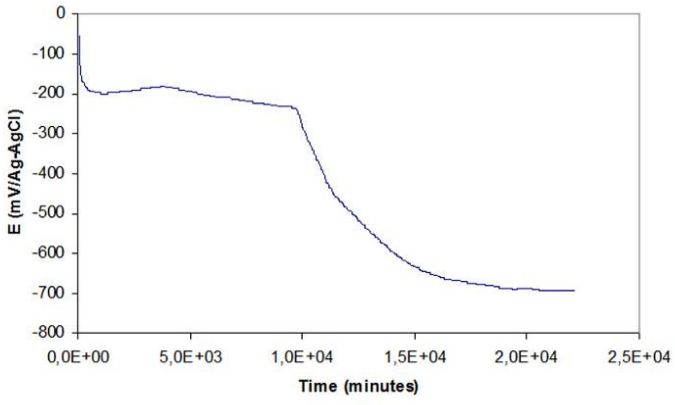



Figure 80: Corrosion potential monitoring of sample 52, in 70% (v/v) PEG 400 solution, after its immersion in 100ppm $NaNO_2$ / 20% (v/v) PEG 400 mixture.

This decrease of $E_{corr}$ over time for sample 141 appears clearly too on figure 81. As regards to the voltammetric plots, the anodic currents for samples 52 to 54 are higher than for the references samples, suggesting that corrosion might happen more readily when bare coupons were previously placed in $NaNO_2$/PEG mixture than not[618].

[618] Note that sample 53 was moved by mistake during the experiment, resulting in its unusable data.

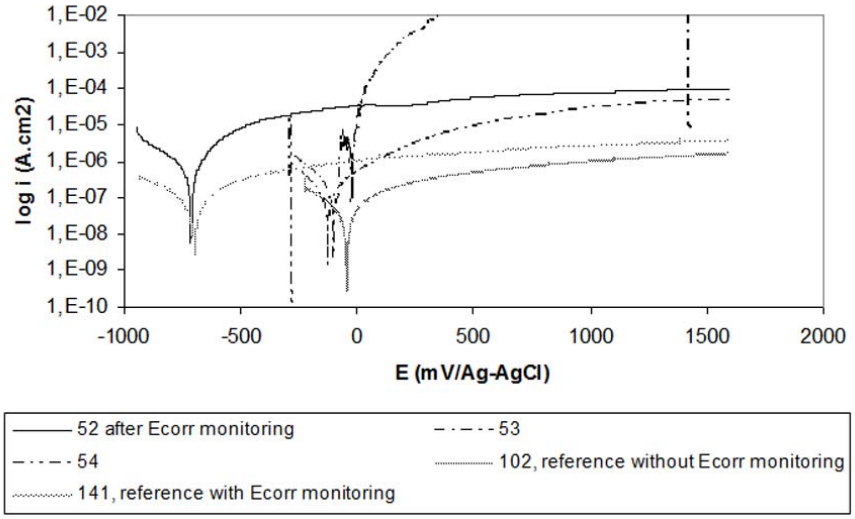



Figure 81: Anodic polarization of bare carbon steel samples in 70% (v/v) PEG 400 solution, after their immersion in 100ppm $NaNO_2$ / 20% (v/v) PEG 400 mixture (samples 52 to 54), scanning rate 1mV/s.

#### 11.2.1.2. CORRODED SAMPLES

The same scheme was performed on corroded carbon steel but on five samples instead of three to once again insure the reproducibility of the electrochemical measurements. Samples 79 to 83 were polarized anodically in 70% (v/v) PEG solution, after their pretreatment in the mixture of 20% PEG 400/100ppm $NaNO_2$. For samples 79 and 80, $E_{corr}$ over time was monitored in 70% PEG solution prior to their polarization. Samples 81 to 83 were polarized directly in this solution. Samples 106 and 124 are still the references coupons. The second one was polarized directly in 70% PEG solution and is therefore to compare to samples 81 to 83. The $E_{corr}$ over time of sample 106 was monitored prior to its polarization in 70% PEG solution. Therefore the behavior of samples 79 and 80 should be compared to sample 106.

The $E_{corr}$ over time of samples 69 and 70 shows that their potential decrease steadily over time. After five days in the 70% (v/v) PEG solution, their potential did not reach yet a stable value (fig.82). This suggests that remaining of $NaNO_2$ at the surface of the samples do not protect them in the highly concentrated PEG solution. For practical reasons, the voltametric measurments were performed after these five days of immersion.

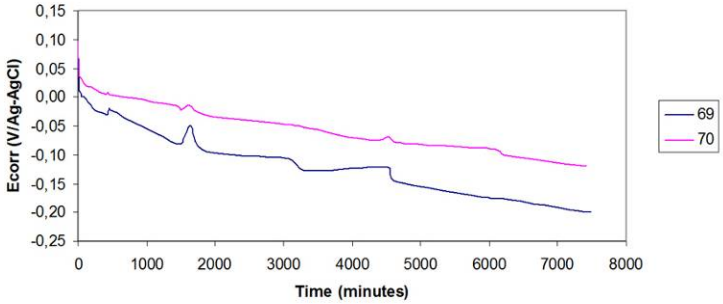



Figure 82: Corrosion potential monitoring of sample 69 and 70, in 70% (v/v) PEG 400 solution, after their immersion in 100ppm $NaNO_2$/ 20% (v/v) PEG 400 mixture.

Figure 83 shows that similarly to samples 69 and 70, $E_{corr}$ of sample 106 before the anodic and cathodic polarizations is lower than for samples directly polarized. Conclusions as regards the efficiency of a pre-treatment in 20% PEG 400 / 100ppm NaNO2 to protect materials exposed to concentrated PEG solutions are difficult to make from these voltammetric curves. The pre-immersion in this solution before the polarization seems to increase the current densities.

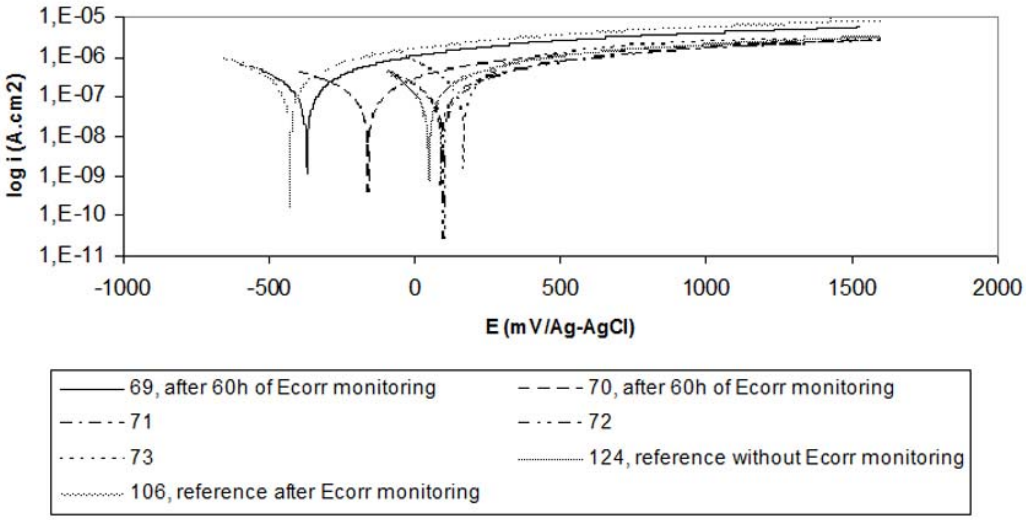
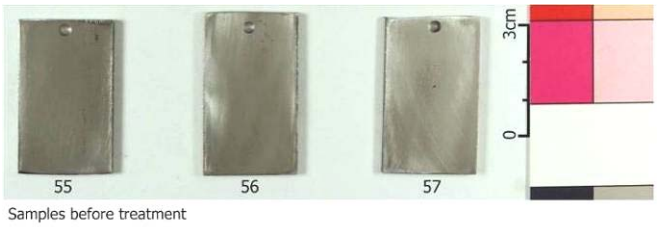



Figure 83: Anodic polarization of corroded carbon steel samples in 70% (v/v) PEG 400 solution, after their immersion in 100ppm $NaNO_2$ / 20% (v/v) PEG 400 mixture (samples 69 to 73).

### 11.2.2. Exposure to a humidity chamber

On bare carbon steel, the following pictures show that samples 55 and 56 did not react well to the humidity chamber test (fig.84). A grey dark layer of corrosion products is noticeable, particularly on sample 55. The same sample already started to corrode while immersed in the mixture of PEG/sodium nitrite (see related section). Also, comparing the effect of $NaNO_2$ to Hostacor IT® in 20% (v/v) PEG 400 solutions, it appears that sodium nitrite at the concentration used, is less effective to protect the metal in the long term. Again, this can be related to the low pH of the $NaNO_2$/PEG mixture and/or to a too low concentration of the nitrite compound.



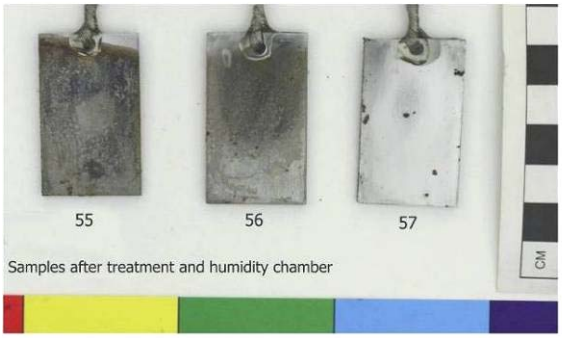



Figure 84: Bare carbon steel samples before treatment and after treatment (immersion in 100ppm $NaNO_2$/ 20% PEG solution) and aging tests in a humidity chambers over 30 days.

On corroded samples, the phenomenon observed on bare metal after accelerated aging is less obvious (fig.85). Nonetheless, the corrosion layers of the samples appeared to be very fragile (tended to flake) after the aging process.


Figure 85: Corroded carbon steel samples before treatment and after treatment (immersion in 100ppm $NaNO_2$ / 20% PEG solution) and aging tests in a humidity chambers over 30 days.

# 12. Corrosion behavior of steel samples in mixtures 20 % (v/v) PEG 400 / carboxylatation solution

As before, the corrosion behavior of the samples is first presented through corrosion potential monitoring plots. A second part of this chapter corresponds to the accelerated aging (voltammetry in concentrated PEG solution and humidity chamber).

## *12.1. Electrochemical behavior of carbon steel in 20 % (v/v) PEG 400/ carboxylatation solution*

The following presentation is also the same as the previous chapters: bare samples' behaviors are presented first, corroded samples are considered afterwards.

### 12.1.1. Bare samples

#### 12.1.1.1. Behavior in carboxylatation solution

During the first hundred minutes, $E_{corr}$ decreased showing a corrosion process (fig.86). This phenomenon is directly followed by a re-increase of $E_{corr}$ indicating the formation of a passive film, certainly constituted of iron carboxylate[619] (fig.86 and 87). This protective film was effective during the first two days (fig.87) but corrosion products (iron carboxylates?) developed on the metal surfaces during seven days of immersion (see pictures in appendix 8). This led eventually to a second decrease of the corrosion potentials. This phenomenon was particularly visible on sample 89 where the solution turned brown. The pH of 3.6 remained stable during the experiment.

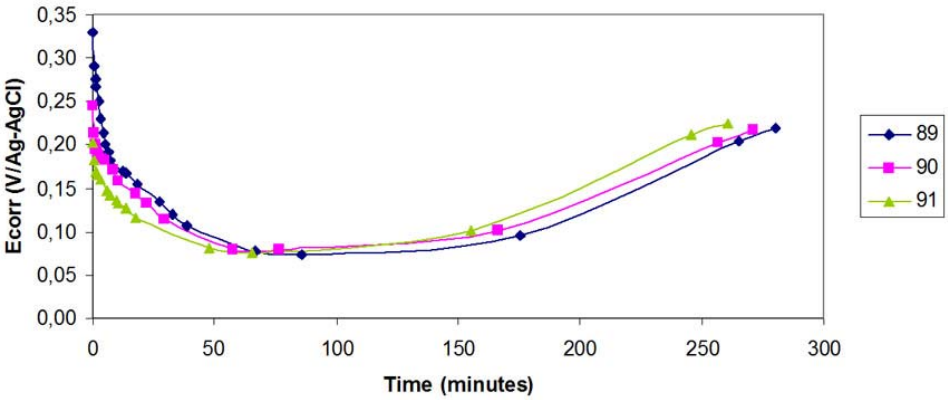



Figure 86: Corrosion potential over time for bare carbon steel samples in carboxylatation solution.

[619] Hollner *et al.*, 2007b, p.66. Hollner names it a « soap » of iron carboxylate (Hollner, written communication, April 2008).

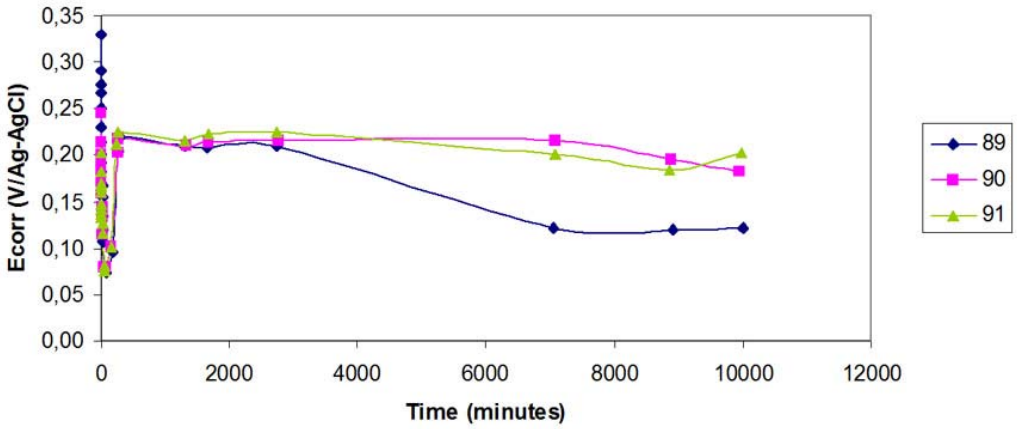



Figure 87: Corrosion potential over time for bare carbon steel samples in carboxylatation solution.

#### 12.1.1.2. BEHAVIOR IN 20% (V/V) PEG 400 / CARBOXYLATATION SOLUTION

Figure 88 shows fluctuactions of $E_{corr}$ values during the first five hours of immersion. Afterwards, the general tendency is that the corrosion potentials goes down, at least during the first two days and tends to get stable over the week of $E_{corr}$ monitoring (fig.89).

Again, corrosion products (iron carboxylates?) formed on the metal surfaces and kept developing during the seven days of immersion. This layer is not fully protective as indicated on several samples where the solution turned brown (samples 92, 93 and 97, see appendix 8).

The pH of 3.9 remained stable.

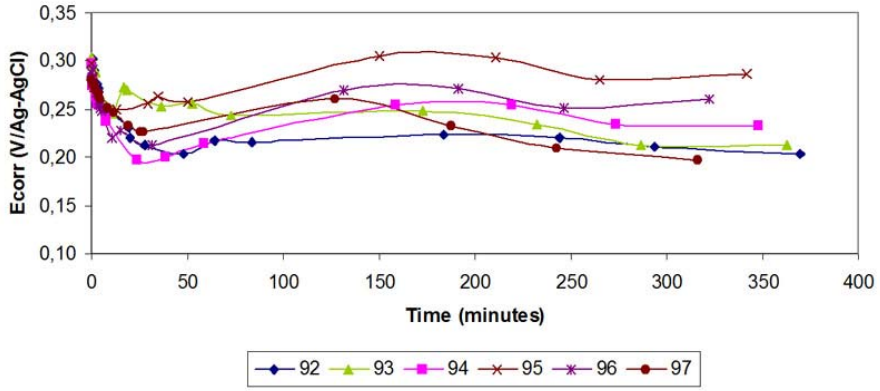



Figure 88: Corrosion potential over time for bare carbon steel samples in 20% (v/v) PEG 400 / carboxylatation soution.

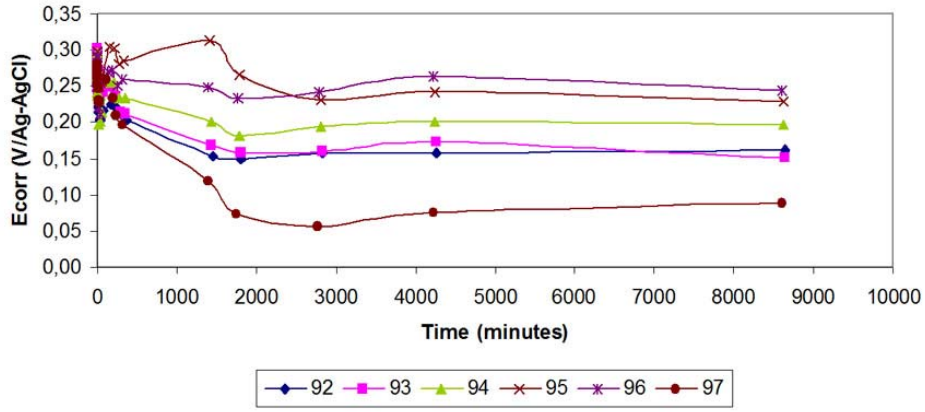



Figure 89: Corrosion potential over time for bare carbon steel samples in 20% (v/v) PEG 400 / carboxylatation soution.

The next experiment consisting in immersing the samples first in carboxylatation solution and in PEG solution afterwards were not performed because these results for bare carbon steel in PEG/ carboxylatation solution were not convincing enough.

### 12.1.2. Corroded samples

#### 12.1.2.1. Behavior in carboxylatation solution

The epoxy placed on the edges of the samples dissolved in the carboxylatation solution allowing bare edges to react during the immersion (for all samples). In such condition, the electrochemical results are not reliable. However, the corroded surfaces did not show further corrosion during the process. Due to the bare edges we should have observed first a decrease of $E_{corr}$ during the first 100 minutes followed by an increase till 300 minutes and a phase of stable values that tends to decrease beyond 3000 minutes. We observed such behaviors on some samples and the presence of the corrosion layers on the metal surface do not seem to modify much the way $E_{corr}$ was changing with time (fig.90 and 91). The corrosion potentials were however slightly higher than for bare samples in the same solution (see fig.87). Even if the solutions in the jars remained quite clear, fragments of the corrosion layers fall down indicating that the remaining material is only slightly affected by the solution (appendix 8 for the referring pictures).

The pH of 3.6 remained stable during the experiment.

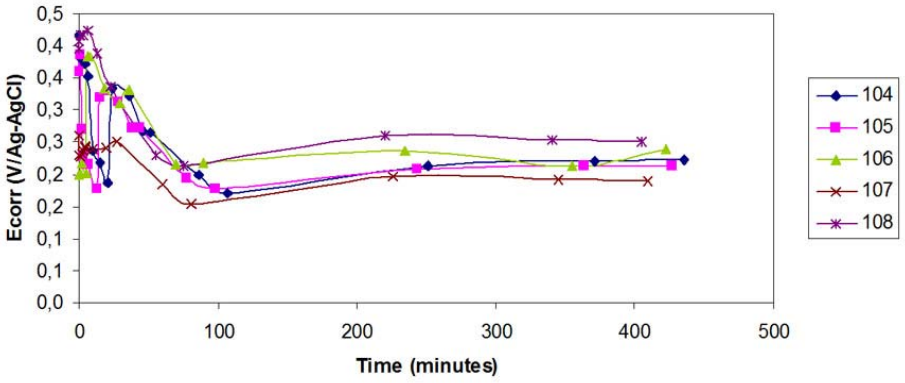



Figure 90: Corrosion potential over time for corroded carbon steel samples in carboxylatation solution.

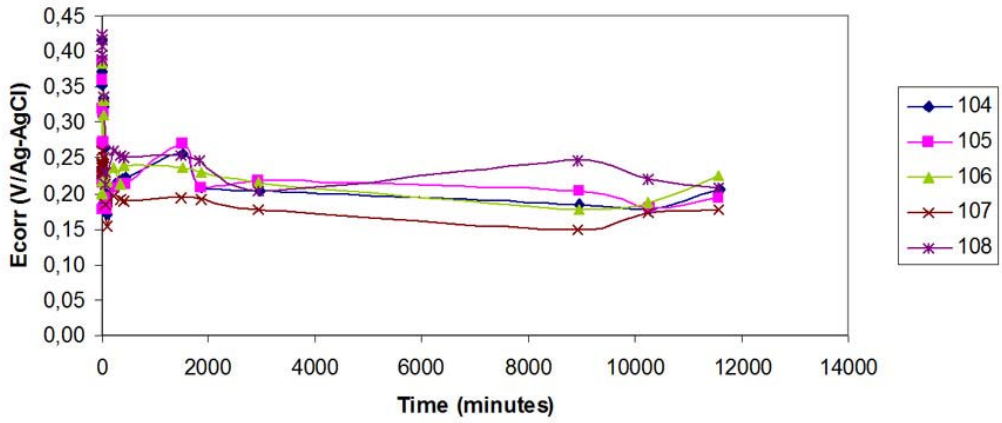



Figure 91: Corrosion potential over time for corroded carbon steel samples in carboxylatation solution.

#### 12.1.2.2. Behavior in 20% (v/v) PEG 400 / carboxylatation solution

For most of the samples, the corrosion potentials tended to increase during the whole length of the experiments, indicating that the surface of the corroded metal samples passivates with time (fig.92 and 93). The values of the potentials are the highest observed until now.

The epoxy still dissolved in the solutions, allowing bare edges to react, the $E_{corr}$ measurements should therefore be interpreted carefully. A thin sediment of corrosion products (or iron carboxylate?) is noticeable at the bottom of the jars.

The pH of the solution changed from 3.9 to 4.3 during the week of immersion.

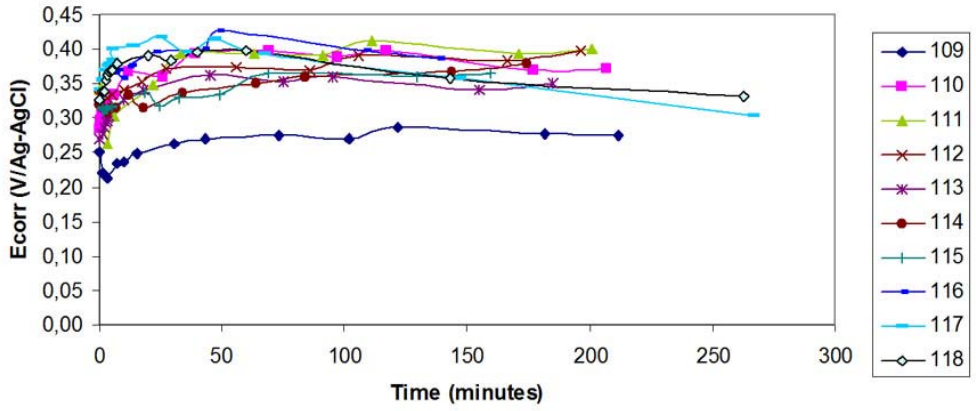



Figure 92: Corrosion potential over time for corroded carbon steel samples in 20%(v/v) PEG 400 / carboxylatation solution.

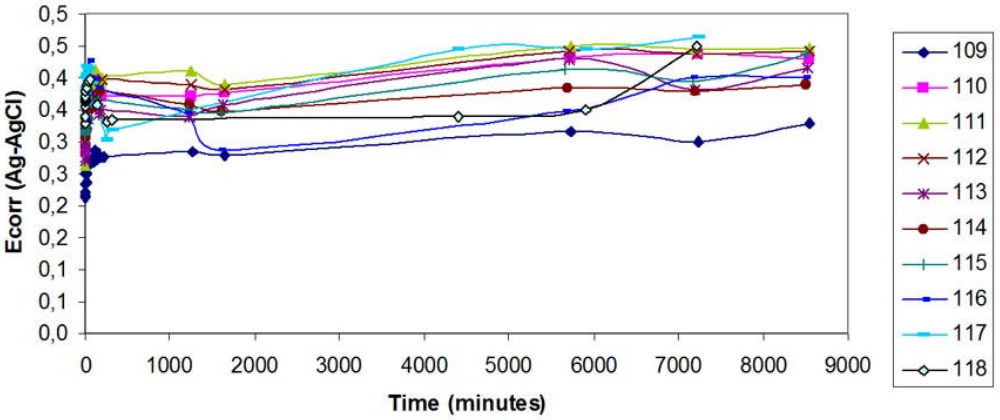



Figure 93: Corrosion potential over time for corroded carbon steel samples in 20%(v/v) PEG 400 / carboxylatation solution.

#### 12.1.2.3. Behavior in carboxylatation solution first, then in 20% (v/v) PEG 400

As for the previous chapters, figure 94 shows the behavior of one of the five samples tested during this experiment. This coupon is representative of the others and treatment photos of all samples are available in appendix 8.

Figure 94 shows high corrosion potential of the sample, indicating a passivation of the coupon while soaked in the carboxylatation solution. When placed in 20% (v/v) PEG 400 afterwards, the samples corroded as the decrease of $E_{corr}$ shows it.

As observed for Hostacor IT® and $NaNO_2$, these experiements showed that a pre-immersion in carboxylatation solution does not protect the samples enough from corrosion when immersed afterwards in PEG solution.

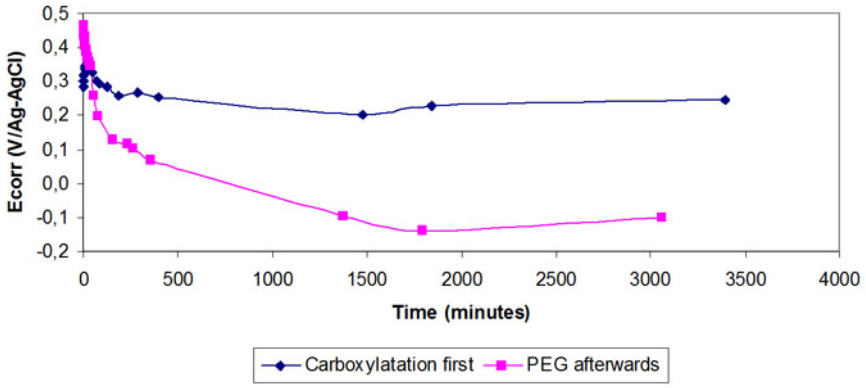



Figure 94: Corrosion potential over time for corroded carbon steel samples first immersed in carboxylatation solution and then in 20%(v/v) PEG 400.

### 12.1.3. Comparison of results

According to the $E_{corr}$ measurements only (fig.95 and 96), the mixture PEG/carboxylatation solution seemed to passivate well both bare and corroded samples: the potentials are between 0.2 and 0.4V/Ag-AgCl. These comparison graphs show that the carboxylatation solution is more effective mixed with PEG than alone, particularly on corroded samples. This can be related to the higher pH of the solution when PEG is present. This suggests though that the carboxylatation solution is compatible with PEG. These promising results on corroded samples should however be considered carefully since the electrochemical measures do not represent the behavior of the corroded surfaces only but also of the one of the bare edges (due to dissolved epoxy resin).

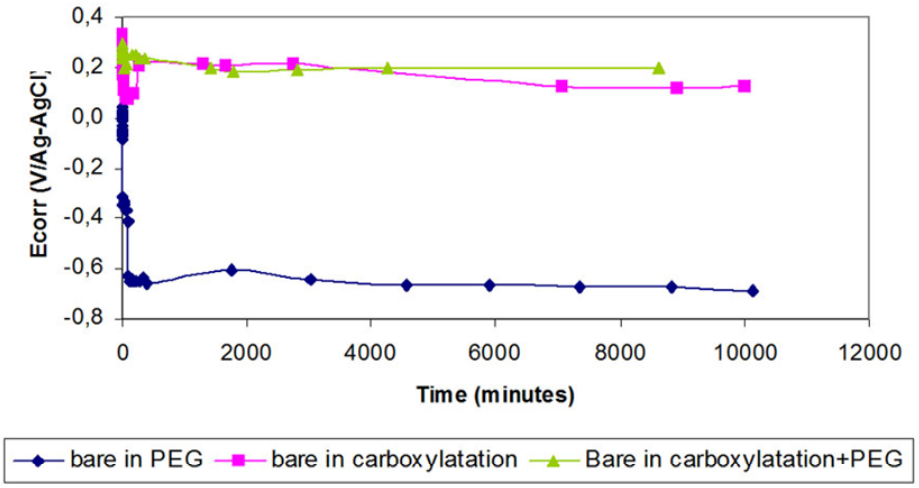



Figure 95: Comparative curves of bare carbon steel in 20% (v/v) PEG 400, carboxylatation solution, and 20% (v/v) PEG 400 / carboxylatation solution.

The observation of the bare samples during treatment showed that this solution is not adapted at all to bare surfaces: local corrosion products (iron carboxylates?) developed on the samples (see appendix 8).

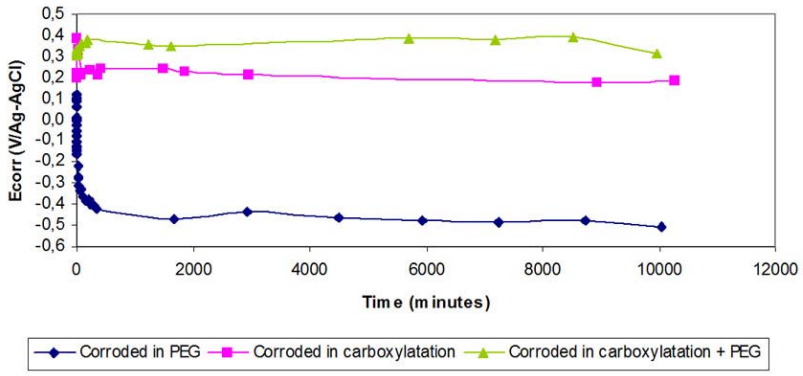



Figure 96: Comparative curves of corroded carbon steel in 20% (v/v) PEG 400, carboxylatation solution and 20% (v/v) PEG 400 / carboxylatation solution.

## *12.2. Accelerated corrosion tests*

### 12.2.1. Voltammetry in concentrated PEG solution: long term effect of PEG on metal

#### 12.2.1.1. BARE METAL

Bare samples 92 to 94 were anodicaly polarized, after their 20% (v/v) PEG/carboxylatation solution treatment. For sample 92, $E_{corr}$ was monitored over time in the 70% (v/v) PEG 400 solution prior to the plarization of the coupon, in the same solution. Samples 93 and 94 were polarized directly. As in chapter 10.2 and 11.2, samples 102 (polarized directly) and 141 (with preliminary monitoring in the concentrated PEG) are references coupons. Therefore, the anodic polarization of samples 93 and 94 should be compared to sample 102 and the one of sample 92 to sample 141. Again, the $E_{corr}$ versus time of sample 141 is not available.

For sample 92, $E_{corr}$ values first decreased rapidly over time (fig.97). A "peak" of potential showed up during the first hundred minutes. Afterwards, the potential decreased steadily. The sudden increase of $E_{corr}$ after few hours of immersion is could be related to remains of corrosion inhibitor at the surface of the sample. The corrosion potential did not really get stable after almost four days but the voltametric plots had to be carried out anyway due to practical reasons.

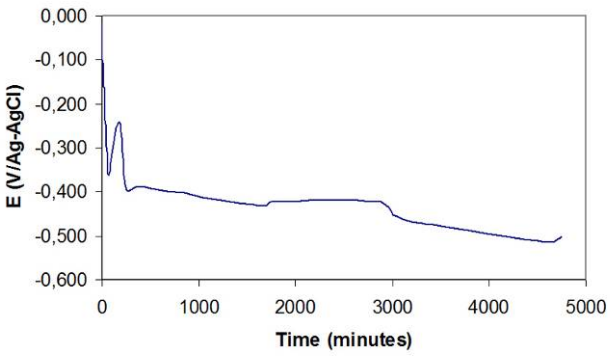



Figure 97: Corrosion potential over time for sample 92, in 70% (v/v) PEG 400 solution, after its immersion in 20% (v/v) PEG 400 / carboxylatation mixture.

Regarding the voltammetric plots, sample 141 presents like sample 92 a lower corrosion potential due to the preliminary immersion in concentrated PEG solution (fig.98). Samples 93 and 94 have a lower corrosion potential than the reference sample 102 showing then a possible effect of the pre-treatment in PEG / carboxylatation mixture.

Voltammetric curves in the anodic region clearly show that a pretreatment in PEG/carboxylatation solution causes an increase of the current densities (with or without a pre-immersion in the concentrated PEG solution)[620].

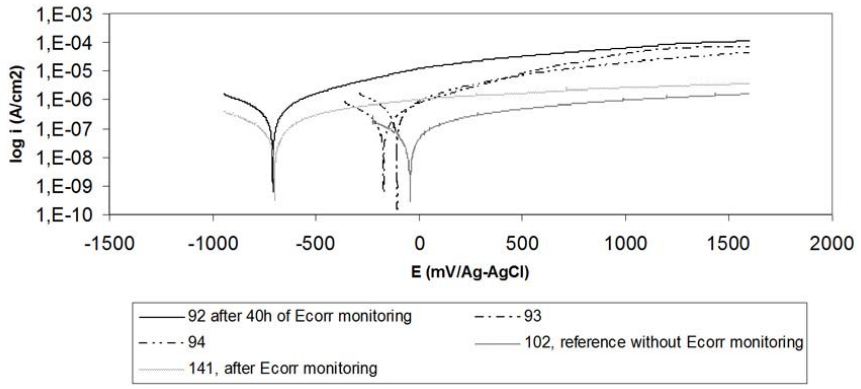



Figure 98: Anodic polarization of bare carbon steel samples in 70% (v/v) PEG 400 solution,
after their immersion in 20% (v/v) PEG 400 / carboxylatation mixture (samples 92 to 94), scanning rate 1mV/s.

#### 12.2.1.2. CORRODED METAL

As for Hostacor® and sodium nitrite, the same experiements were performed on five corroded carbon steel. Samples 109 to 113 were polarized anodically in 70% (v/v) PEG solution, after their pretreatment in the mixture of 100ppm $NaNO_2$ / 20% PEG 400. For samples 109 and 110, $E_{corr}$ versus time was monitored in 70% PEG solution prior to their polarization. Samples 111 to 113 were polarized directly. Samples 106 and 124 were still the references coupons. The second one was polarized directly in 70% PEG solution and is therefore to compare to samples 111 to 113. $E_{corr}$ over time was monitored for sample 106 prior to its polarization in 70% PEG solution. Therefore the behavior of samples 109 and 110 should be compared to sample 106.

The $E_{corr}$ monitoring of samples 109 and 110 shows that their potentials decreased steadily whitout stabilizing after five days of immersion in 70% PEG solution (fig.99). However, according to the voltammetric plotes, their $E_{corr}$ does not really differ from sample 106 which did not receive any pre-treatment (fig.100).

[620] Note that sample 53 was moved by mistake during the experiment, resulting in its unusable data.

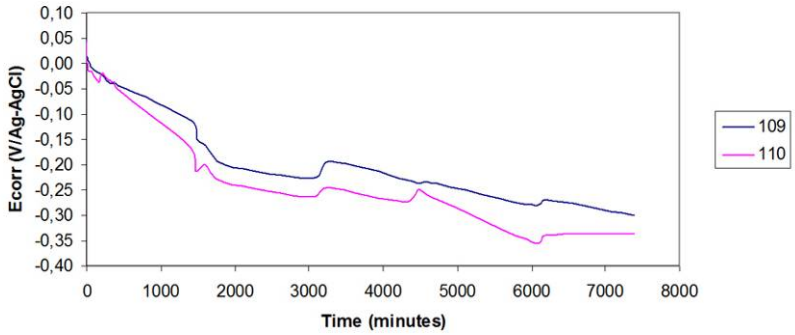



Figure 99: Corrosion potential monitoring of samples 109 and 110, in 70% (v/v) PEG 400 solution, after their immersion in 20% (v/v) PEG 400 / carboxylatation mixture.

The study of these curves shows that a pre-immersion of the corroded samples in the concentrated PEG solution tends to increase the anodic current densities (fig.100). No conclusion can really be made as regards the effect of the pretreatment in 20% PEG 400/carboxylatation solution on the corrosion behavior in concentrated PEG solutions.

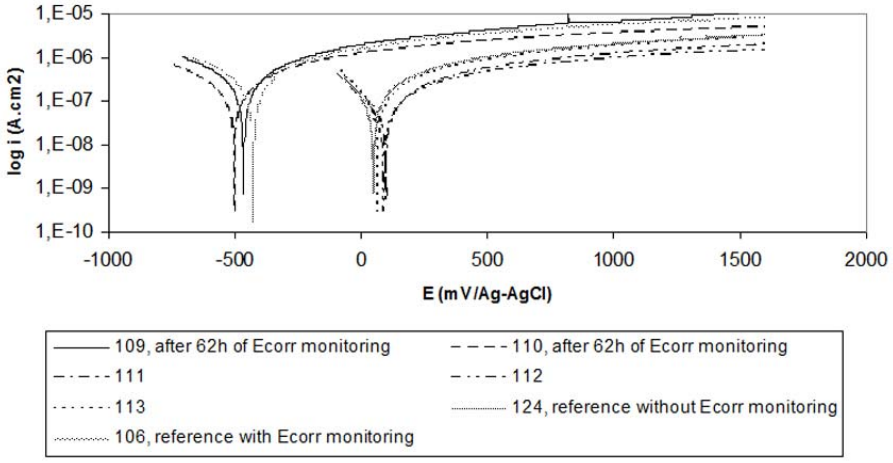



Figure 100: Anodic polarization of corroded carbon steel samples in 70% (v/v) PEG 400 solution, after their immersion in 20% (v/v) PEG 400 / carboxylatation mixture (samples 109 to 113), scanning rate 1mV/s.

### 12.2.2. Exposure to a humidity chamber

No picture of the bare samples at the end of the pre-treatment PEG/carboxylatation solution was made making comparison before and after the exposure to the humidity chamber difficult. Therefore the effect of the corrosion products formed during the pre-treatment on the corrosion progress during the exposure to the humid chamber is unknown (fig.101).

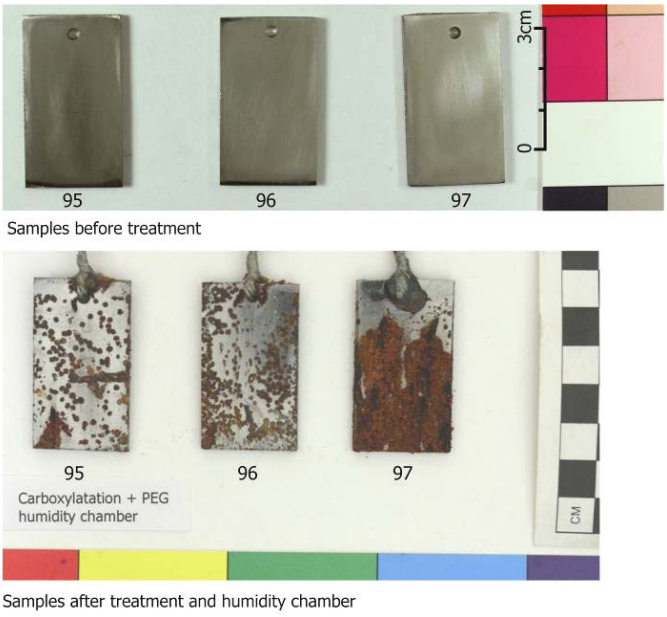



Figure 101: Bare carbon steel samples before treatment and after treatment (immersion in 20% PEG/ carboxylatation solution) and aging tests in a humidity chambers over 30 days.

On corroded metal, the samples resisted well to the humidity variations. The corrosion layer did not flake more than before the aging and further corrosion was not observed[621]. New corrosion products are visible on the edges of the samples where the epoxy resin was dissolved (fig.102).

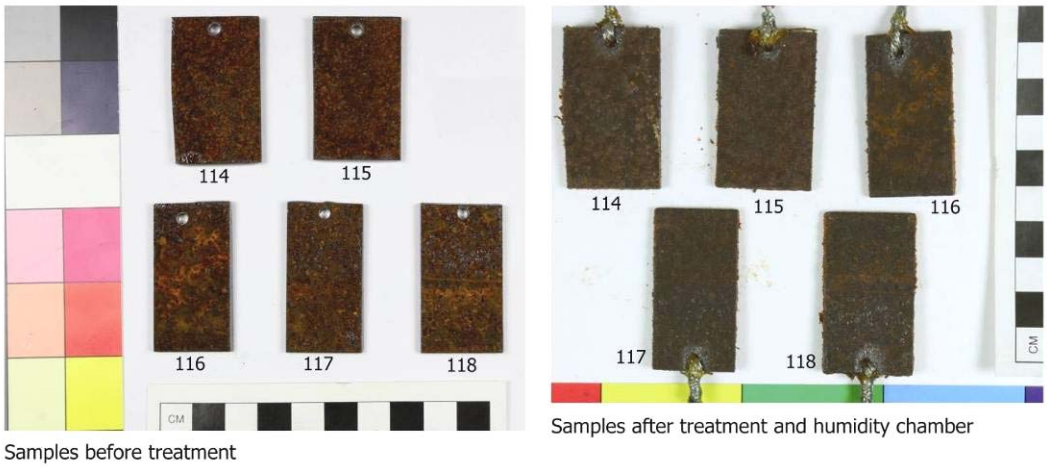



Figure 102: Corroded carbon steel samples before treatment and after treatment (immersion in 20% PEG/ carboxylatation solution) and aging tests in a humidity chambers over 30 days.

[621] Photos after the immersion in 20%PEG 400/carboxylatation solution are also missing.

# 13. Corrosion behavior of steel samples in mixtures 20 % (v/v) PEG 400 / 0.05M $NaC_{10}$

As discussed in chapter 7.2, sodium decanoate was only tested on bare metal because it has been demonstrated that its performances were significantly diminished on corrosion layers[622].

## *13.1. Electrochemical behavior of carbon steel in 20 % (v/v) PEG 400/ 0.05M $NaC_{10}$*

### 13.1.1. Behavior in 0.05M $NaC_{10}$ in water

$E_{corr}$ over time monitoring for the three samples do not give reproducible values (fig.103 and 104). After five days of immersion (around 8000 minutes), $E_{corr}$ tended to get stable at around -0.04 and -0.06V/Ag-AgCl. We could consider that the corrosion potentials are almost stable and that corrosion does not proceed. This is confirmed by the surface appearance of the samples and the aspect of the solutions (see appendix 9 for the pictures[623]). The pH of the solution stayed stable during the experiment (7.2 during two weeks).

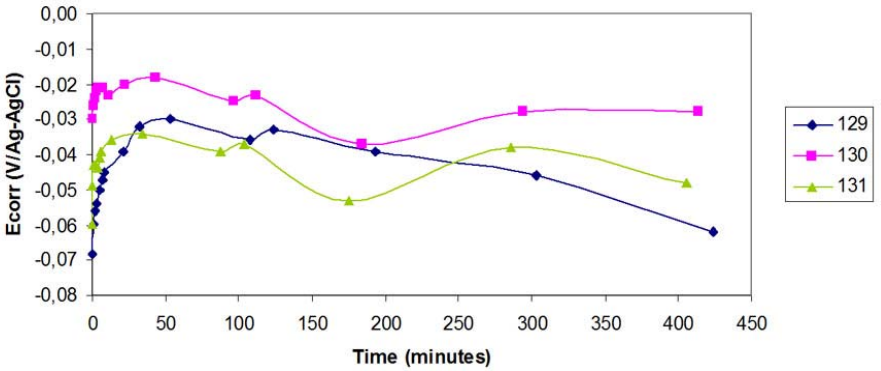



Figure 103: Corrosion potential over time for bare carbon steel samples in $NaC_{10}$ solution.

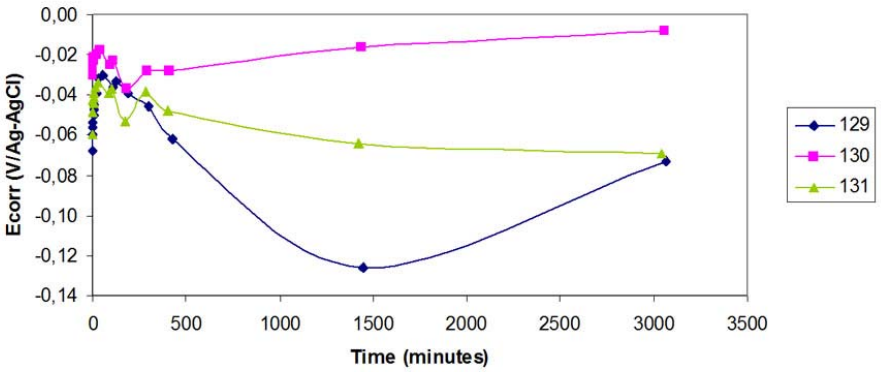



Figure 104: Corrosion potential over time for bare carbon steel samples in $NaC_{10}$ solution.

[622] Hollner, 2007b, p.66.

[623] In appendix 9, note that the solutions have a white aspect. This is the original color of the solution and not related to the samples immersion.

### 13.1.2. Behavior in 20% (v/v) PEG 400 / 0.05M $NaC_{10}$

In this mixture, the electrochemical measurements were more or less reproducible (fig.105 and 106). The $E_{corr}$ values showed a rapid increase during the first hundred minutes of immersion. The potentials remained then more or less stable during the six days of measurements. $NaC_{10}$ appeared to protect well the bare samples in 20% (v/v) PEG solution. The pH of the solution stayed stable (7.3) during two weeks.

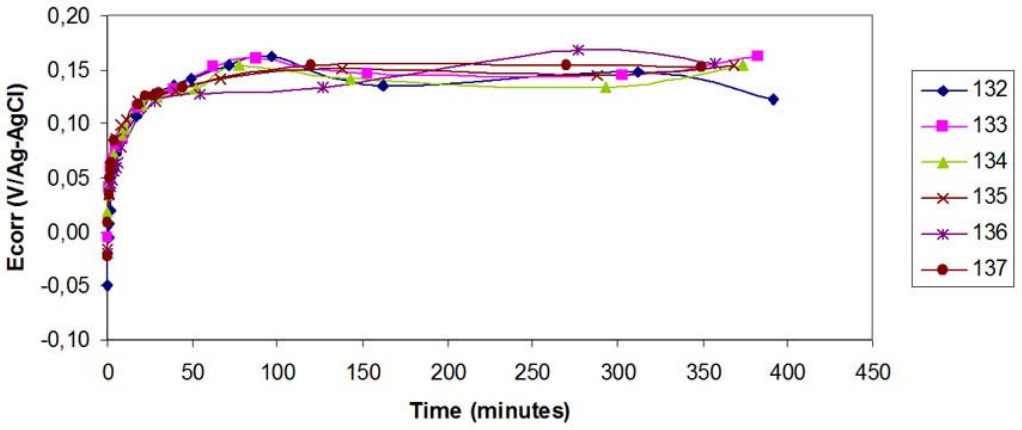



Figure 105: Corrosion potential over time for bare carbon steel samples in 20% (v/v) PEG 400 / 0.05M $NaC_{10}$.

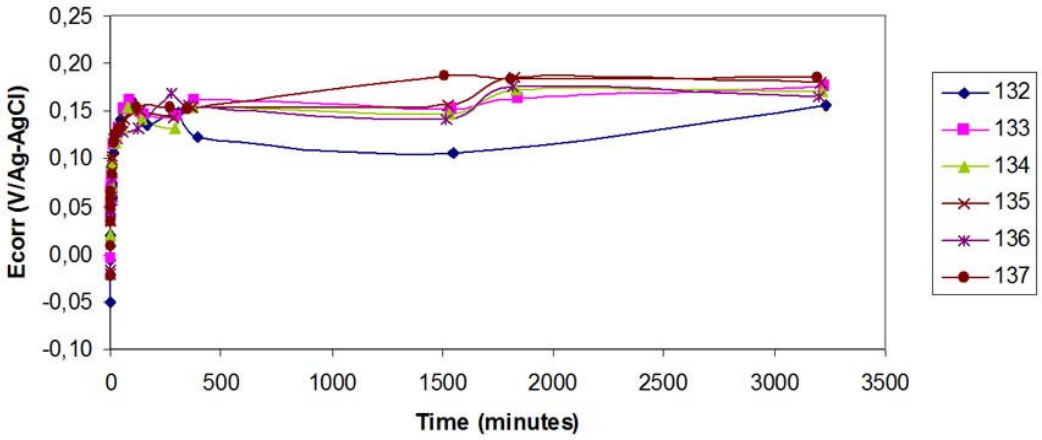



Figure 106: Corrosion potential over time for bare carbon steel samples in 20% (v/v) PEG 400 / 0.05M $NaC_{10}$.

### 13.1.3. Behavior in 0.05M $NaC_{10}$ first, then in 20% (v/v) PEG 400

The behavior of only one sample is presented below and summarizes the reaction of the three bare coupons tested (fig.107).

During the first immersion of the samples in sodium decanoate solution, the $E_{corr}$ values increased slightly showing the passivation of the metal. When the samples where placed in 20% PEG 400 solution afterwards, the fast decrease of potentials showed that the samples corroded. Therefore, the protective film formed at the surface of the carbon steel during the immersion in 0.05M $NaC_{10}$ is not strong enough to protect the metal in a solution of PEG afterwards.

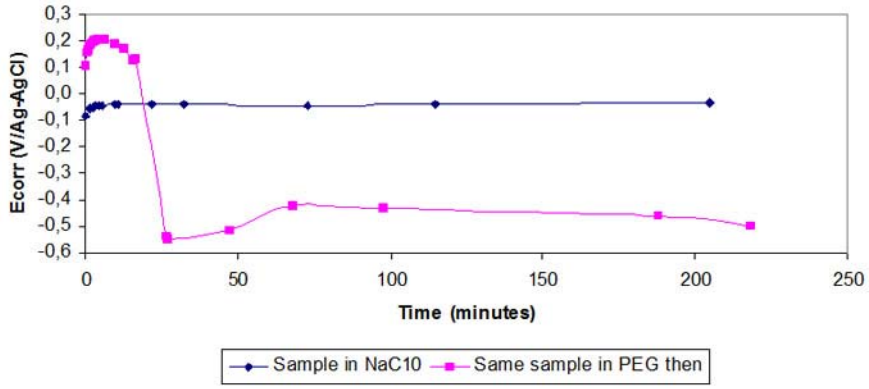



Figure 107: Corrosion potential over time for bare carbon steel samples first immersed in 0.05M $NaC_{10}$ solution and in 20%(v/v) PEG 400 afterwards.

### 13.1.4. Comparison of results

According to these trials, sodium decanoate can be considered effective to protect bare carbon steel in 20% (v/v) PEG 400 solution. As for Hostacor IT®, sodium nitrite and carboxylatation solutions, the protection of the bare samples is higher in PEG solution than with the inhibitor it self (fig.108).

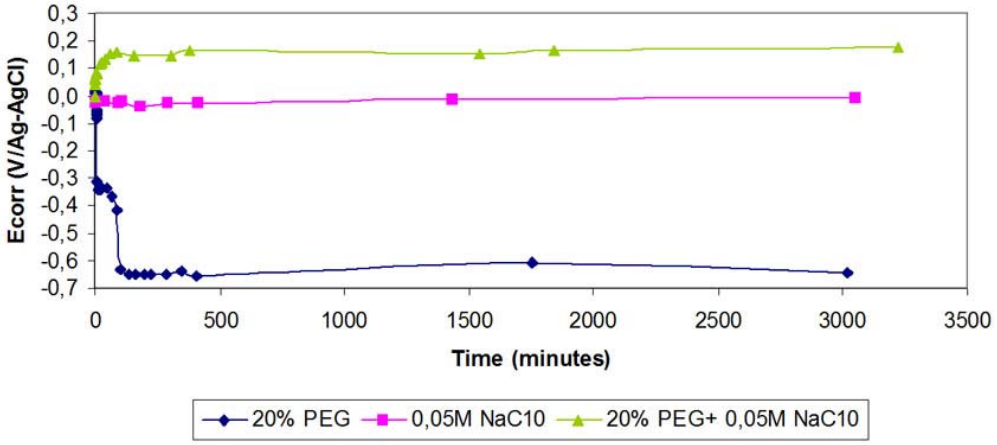



Figure 108: Comparative curves of bare carbon steel in 20% (v/v) PEG 400, 0.05M $NaC_{10}$ solution, and 20% (v/v) PEG 400 / 0.05M $NaC_{10}$ solution.

## *13.2. Accelerated corrosion tests*

### 13.2.1. Voltammetry in concentrated PEG solution: long term effect of PEG on metal

Bare samples 132 to 134 were anodically polarized, after their PEG 400 / 0.05M $NaC_{10}$ solution treatment. For sample 132, $E_{corr}$ was monitored over time, in the 70% (v/v) PEG 400 solution, prior to the polarization of the coupon, in the same solution. Samples 133 and 134 were polarized directly in the same solution. Samples 102 (with direct polarization in 70% PEG) and 141 (with a pre-immersion in 70% PEG) were still references coupons. The anodic polarization of samples 133 and 134 should be compared to the one of sample 102 and the anodic polarizarion of sample 92 to the one sample 141.

For sample 132, $E_{corr}$ versus time monitoring shows a corrosion behavior in two steps (fig.109). The first slow decrease could be due to $NaC_{10}$ remains and the second would show the re-start of the corrosion progress (fig.109). Afterwards, the potential decreases steadily over time.

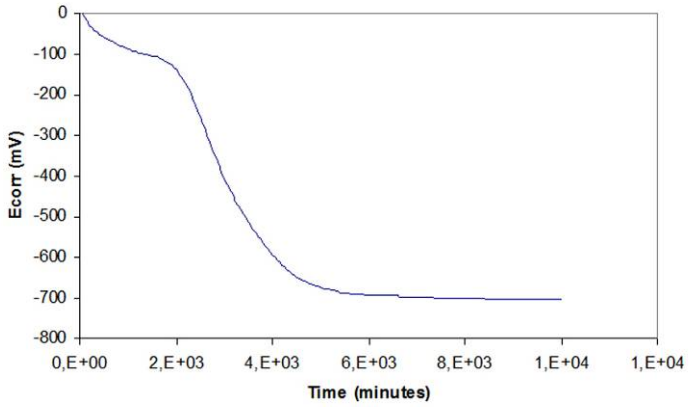



Figure 109: Corrosion potential monitoring of sample 132, in 70% (v/v) PEG 400 solution, after its immersion in 20% (v/v) PEG 400 / 0.05M $NaC_{10}$ mixture.

Figure 110 shows that due to its pre-immersion in concentrated PEG solution, sample 141 has a similar corrosion potential to sample 132 before the anodic and cathodic polarizations. When referring to the anodic polarizations, the current densities are higher for samples 132 and 134 than for the references samples (fig.110). This suggests that corrosion could happen more readily on the samples immersed prior in the 20% (v/v) PEG 400 / 0.05M NaC10 than when no pre-treatment was made.

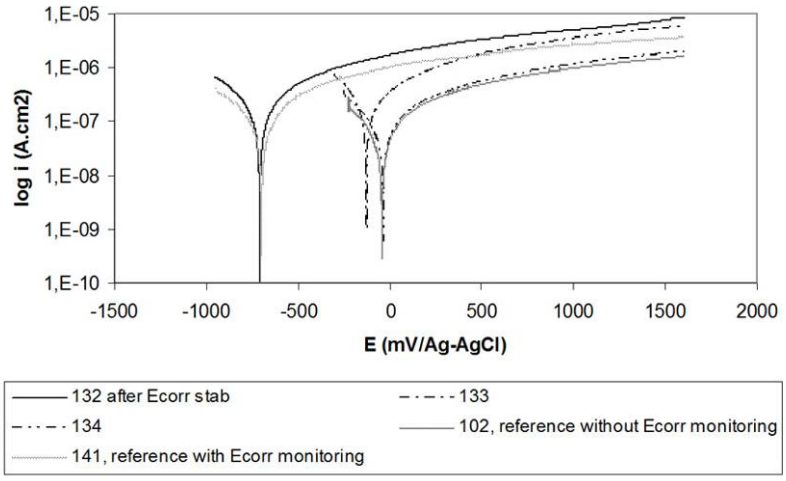
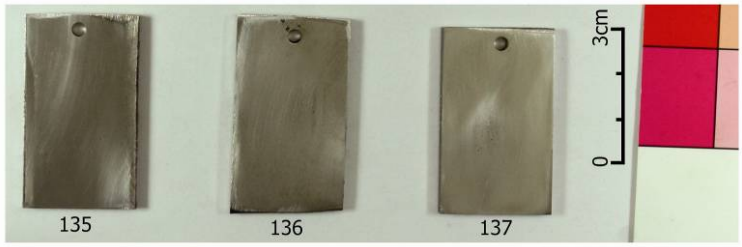


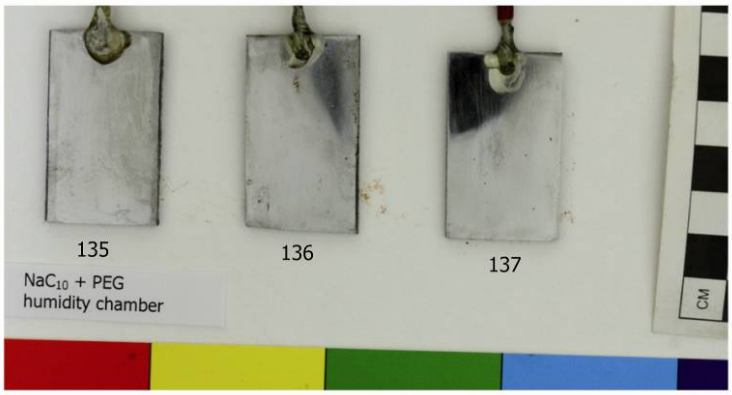

Figure 110: Anodic polarization of bare carbon steel samples in 70% (v/v) PEG 400 solution, after their immersion in 20% (v/v) PEG 400 / 0.05M $NaC_{10}$ mixture (samples 132 to 134), scanning rate 1mV/s.

### 13.2.2. Exposure to a humidity chamber

The aging made after soaking the samples in a mixture of 0.05M $NaC_{10}$ and 20% (v/v) PEG solution, did not affect the surface of the bare metal (fig.111). The sodium decanoate seems to protect the metal even in an uncontrolled environment[624].




Samples before treatment




Samples after treatment and humidity chamber

Figure 111: Bare carbon steel samples before treatment and after treatment (immersion in 20% PEG/ 0.05M $NaC_{10}$ solution) and aging tests in a humidity chambers over 30 days.

[624] A mistake was made on the "after treatment" photo: the wrong side of sample 136 is visible comparing to the "before treatment" picture.

# 14. Synthesis

The experiments carried out within this project provided information about the ability of the selected corrosion inhibitors to protect carbon steel in PEG solutions. None of the corrosion inhibitors were able to prevent corrosion in PEG during the two steps treatments. These results will not be discussed further. However, these chemicals had various inhibitive effects when applied alone or in combination with PEG. This is summarized in the following chapter.

A first section will discuss samples treated in corrosion inhibitors alone. The second part will review the results obtained for the mixtures PEG / corrosion inhibitor, including those of the accelerated aging tests.

## *14.1. Behavior of carbon steel in each corrosion inhibitor*

Figure 112 compares the results of the $E_{corr}$ over time monitoring for samples of bare carbon steel immersed in each inhibitive solution (fig.112). The carboxylatation solution at the concentration used, seems to give the best protection on bare metal as it has the highest $E_{corr}$ values. However, note that the $E_{corr}$ for the carboxylatation decreases over two days. The aqueous solution of $NaNO_2$ (100ppm) is the second most effective protective compound for bare metal surfaces, followed by the sodium decanoate (in that case the potentials remain almost constant), and Hostacor IT®.

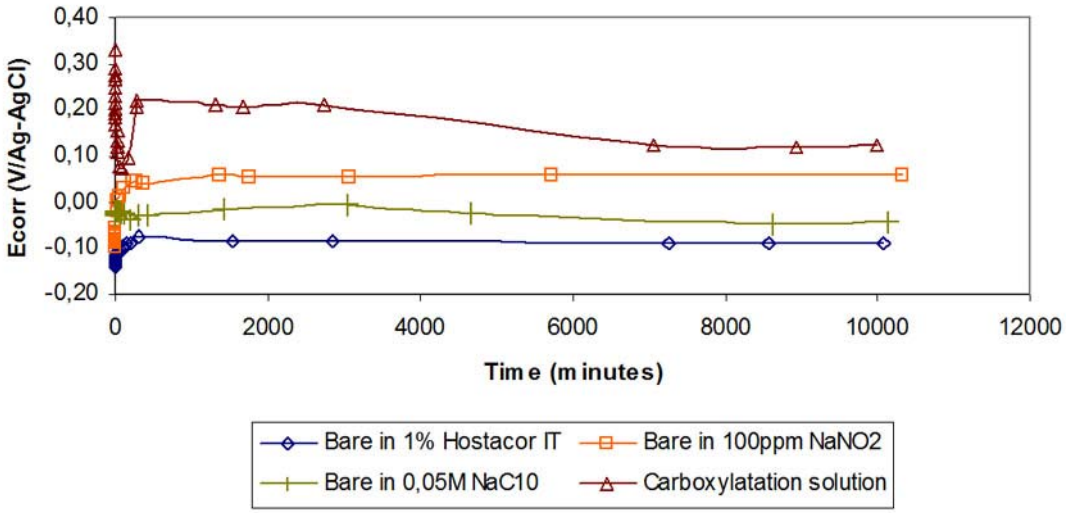



Figure 112: $E_{corr}$ monitoring over seven days for bare carbon steel, in 1% (v/v) Hostacor IT®, 100ppm $NaNO_2$, carboxylatation solution and 0.05M $NaC_{10}$ in deionized water.

Similar conclusions were achieved for corroded metal surfaces. Once again the carboxylatation solution seems to be the most effective, followed by $NaNO_2$ and Hostacor IT® (fig.113). Sodium decanoate was not evaluated here since it is known to be ineffective on corroded surfaces.

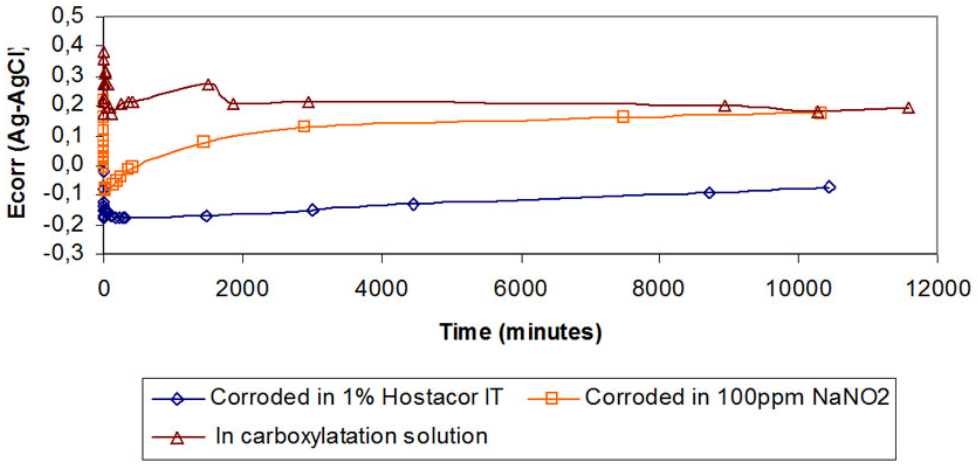



Figure 113: $E_{corr}$ monitoring over seven days for corroded carbon steel, in 1% (v/v) Hostacor IT®, 100ppm $NaNO_2$, carboxylatation solution and 0.05M $NaC_{10}$ in deionized water.

The next table compares the other parameters taken into account during the experiments (table 2).

| Solutions and metal | | pH | Aspect of the solution | Features of the metal surfaces after immersion |
|---|---|---|---|---|
| 1% Hostacor IT ® in deionzed water | Bare | 8.1, stable | - | - |
| | Corroded | 8.1, stable | - | - |
| 100ppm $NaNO_2$ in deionized water | Bare | 6.6, stable | - | - |
| | Corroded | 6.6, stable | Discoloration of 2 solutions out of 6 | - |
| Carboxylatation solution | Bare | 3.6, stable | Discoloration of all solutions | Corrosion products (or iron carboxylate?) |
| | Corroded | 3.6, stable | Solutions clear but corrosion products at the bottom of the jars | Epoxy resin dissolved during treatment exposing bare edges to the solution |
| 0.05M $NaC_{10}$ in deionized water | Bare carbon steel | 7.2, stable | - | - |

Table 2: pH of the solutions and particular observations made on bare and corroded carbon steel samples, during and after treatement, in 1% (v/v) Hostacor IT®, 100ppm $NaNO_2$, carboxylatation solution and 0.05M $NaC_{10}$ in deionized water.

This table shows that the carboxylatation solution is the most acidic. Although the monitoring of the corrosion potential over time shows a passivation phenomenon, after a few days some corrosion products developed on the metal surface that are not protective. This is demonstrated by a corresponding decrease in potential. It is important to note here that this solution was not developed for bare metal but for corroded surfaces[625]. However, the results obtained on corroded metal are compromised since the solution dissolved the epoxy resin applied on the edges.

[625] Hollner *et al.*, 2007b, p.66.

Sodium nitrite is then the most suitable compound to protect both bare and corroded metal surfaces. It is followed by sodium decanoate on bare metal surfaces and Hostacor IT® for both bare and corroded metal surfaces.

## *14.2. Behavior of carbon steel in 20% (v/v) PEG 400 / inhibitors mixtures*

The next graphic (fig.114) presents the corrosion potentials, monitored over one week, for bare carbon steel in the different corrosion inhibitors added to 20% (v/v) PEG 400 solutions.

On bare carbon steel, the 20% PEG/sodium nitrite mixture gives the highest corrosion potentials of all the solutions. This suggests that $NaNO_2$ is more effective for bare metal protection in PEG than Hostacor® or other carboxylates.

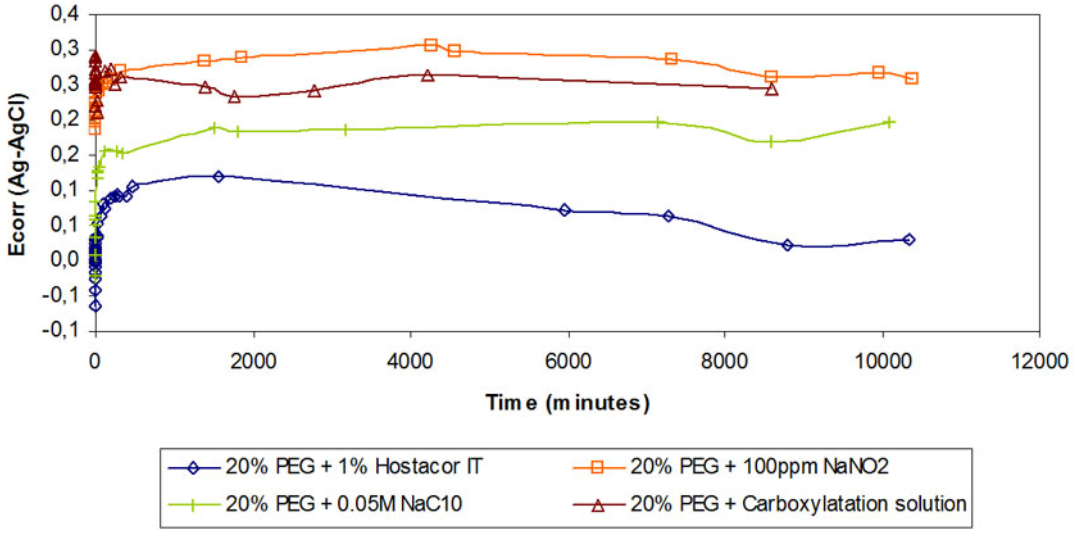



Figure 114: $E_{corr}$ monitoring over seven days for bare carbon steel, in 20% (v/v) PEG 400/ corrosion inhibitor mixtures.

On corroded surfaces, the highest corrosion potentials were obtained in the 20% (v/v) PEG 400 / carboxylatation solution mixture (fig.115 and 116). This time, sodium nitrite appeared to be less protective than Hostacor IT® (lower $E_{corr}$ values).

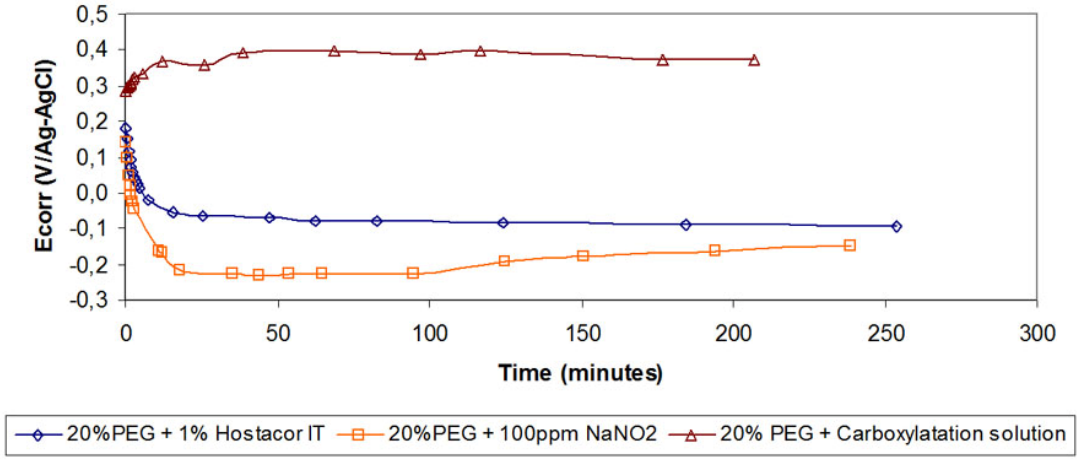



Figure 115: $E_{corr}$ monitoring over few hours for corroded carbon steel, in 20% (v/v) PEG 400/ corrosion inhibitor mixtures.

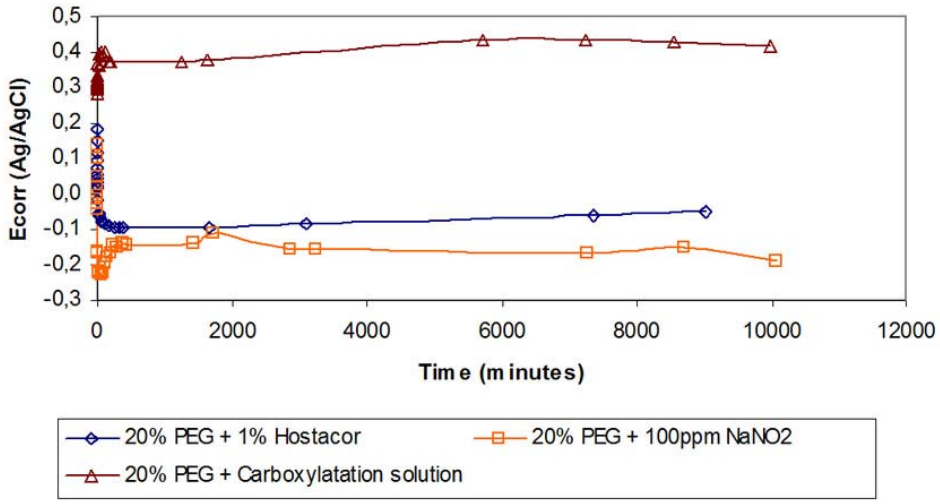



Figure 116: $E_{corr}$ monitoring over seven days of corroded carbon steel, in 20% (v/v) PEG 400/ corrosion inhibitor mixtures.

Interpretations of $E_{corr}$ measurments can be improved by discussing other parameters such as pH variations, features of the metal surfaces after treatment, aspect of the solution, and results of the accelerated aging. This is summarized in table 3.

The high corrosion potentials observed for bare carbon steel in the PEG/$NaNO_2$ solution did not prevent superficial tarnishing of the samples. This issue can be related to the low pH of the mixture. Also the PEG/$NaNO_2$ solution for corroded samples created a higher range of pH. These changes in pH might also explain the relatively low $E_{corr}$ values recorded during the experiment (fig.115). The PEG/$NaNO_2$ mixture did not provide promising in the long term protection. Instead the preexisting corrosion products became friable and detached from the surface after treatment in the humidity chamber. The voltammetric plots showed no particular effect from pretreating the corroded samples in PEG/$NaNO_2$.

Samples treated in PEG/Hostacor® solution were pH stable and did not have any surface tarnishing nor growth of corrosion products. However, both bare and corroded coupons had little resistance to polarization in concentrated PEG solution. The humidity chamber tests also increased corrosion.

The phenomenon of corrosion product deposits was observed for bare coupons placed in PEG/ carboxylatation solution. Despite the fact that the edges of the corroded samples were not fully protected with epoxy resin after immersion, their surfaces did not tend to corrode when polarized in concentrated PEG solution, nor after thirty cycles in the humidity chamber.

Lastly, the bare samples treated in PEG/$NaC_{10}$ solution were resistant to the uncontrolled environment but not to a polarization in concentrated PEG solution.

| Solutions and metal | | pH | Features of the metal surfaces after treatment and aspect of the solution | Behavior in concentrated PEG solution (voltammetry) | Particularities of the samples after the humidity chamber tests |
|---|---|---|---|---|---|
| 20% (v/v) PEG 400 / 1% Hostacor IT ® | Bare | 8, stable | - | Corrosion favored | - |
| | Corroded | 8, stable | - | Corrosion favored | Corrosion products flaking slightly |
| 20% (v/v) PEG 400 /100ppm $NaNO_2$ | Bare | 4.2, stable | Tarnishing of 3 samples out of 6 and discoloration of the solutions for 2 samples | Corrosion favored | Tarnishing of 2 samples out of 3 |
| | Corroded | 4.2 first and 4.6 or 5.2, depending on the samples, after two weeks | - | Corrosion neither favored nor slowed | Corrosion products flaking |
| 20% (v/v) PEG 400 / carboxylatation solution | Bare | 3.6, stable | Corrosion products (or iron carboxylate?) and discoloration of 3 solutions out of 6 | Corrosion favored | Corrosion products (or iron carboxylate ?) still covering the surfaces |
| | Corroded | From 3.9 to 4.3 | Corrosion products on the edges (or iron carboxylate?) and thin layer of corrosion prod. at the bottom of the jars | Corrosion neither favored nor slowed | - |
| 20% (v/v) PEG 400 / 0.05M $NaC_{10}$ | Bare | 7.2, stable | - | Corrosion favored | - |

Table 3: Parameters taken into account (in addition to the $E_{corr}$ monitoring) to assess the effectiveness of the corrosion inhibitors in PEG solution: comparison for bare and corroded carbon steel in each solution.

Considering the treatment of samples in PEG and Hostacor® solution, the pH were stable, the surfaces of the samples did not present any tarnishing or corrosion products, but both bare and corroded coupons seemed weakened by this first immersion since they did not resist well to a polarization in concentrated PEG solution. The humidity chamber tests also increased corrosion.

When bare coupons were placed in a mixture of PEG and carboxylatation solution, the same phenomenon of corrosion products (iron carboxylates?) deposit was observed. For corroded sample, despite the fact that their edges were not protected any more with epoxy resin after immersion, their

surfaces did not show propensity to further corrosion neither polarized in concentrated PEG solution, nor after thirty humidity cycles.

Laslty, the bare samples treated in PEG/$NaC_{10}$ solution, were resistant to the uncontrolled environment but not to a polarization in concentrated PEG solution.

# 15. Discussion

This study allowed a comparison of the effectiveness of 1% (v/v) Hostacor IT®, 100ppm $NaNO_2$, carboxylatation and 0.05M $NaC_{10}$, in aqueous solutions on bare and corroded carbon steel samples. The corrosion potential over time monitoring seemed to suggest that the carboxylatation solution is the most effective inhibitor to protect the materials. The fact that this solution was not adapted to bare carbon steel is actually not surprising, since this mixture has been developed to protect corroded metal[626]. In addition, the carboxylatation solution has not been designed to treat iron by immersion but to be applied with a brush. This is the reason why this solution is so acidic and contains an oxidant: it must form a protective layer on corrosion products during a short application period. Due to the aggressiveness of the solution, the bare samples were readily covered by corrosion products (iron carboxylate?) while the epoxy resin protection layer on the corroded samples was totally dissolved by long immersion in the solution.

On the other hand, a 100ppm sodium nitrite solution seems to be the best compromise to protect steel in aqueous solutions. This mixture could therefore provide a good storage environment for iron/waterlogged wood. If its ability to reduce galvanic corrosion is proved, sodium nitrite could even be a good storage solution for more complex composites such as large objects from the USS *Monitor*. However, further research is required notably into assessing whether or not the sodium nitrite has an effect on wood[627].

Interesting results appeared from samples first soaked in the corrosion inhibitor solutions prior to an immersion in 20% PEG 400. It appeared that none of the inhibitor treated samples were protected enough to be passivated in PEG afterwards. This result is interesting with regards to the treatment of artifacts since if an artifact is immersed in PEG solution (only), after an inhibitive storage solution, the metallic compounds will corrode.

The results for the effectiveness of corrosion inhibitors in PEG solution are interesting as well.

The compatibility of carboxylate based solutions (carboxylatation solution and sodium decanoate), with PEG seemed good. No sever pH fluctuations were recorded during trials. It is however not

[626] Hollner *et al.*, 2007 a and b.

[627] CC Technology, INC., 2007.

surprising that carboxylation solution and sodium decanoate are compatible with PEG, since Hostacor® is another carboxylate based inhibitor and was especially designed to be compatible with glycols[628].

According to the high $E_{corr}$ values, carboxylatation solution presented the best inhibitive effect of all solutions tested. However, treating a non-separable iron/wood composite with this solution would damage the wooden part due to the acidic pH.

The sodium decanoate showed better inhibitive performance than Hostacor IT® on bare samples. These results are very interesting considering that sodium carboxylates' family is effective in protecting several metal alloys[629]. However, if thick corrosion layers on iron/wood objects prevent the use of $NaC_{10}$, one of its "brothers" may be interesting for copper/waterlogged wood composites. Rocca and Mirambet demonstrated that $NaC_7$ was the best carboxylate for copper alloys[630]. Further tests would be required to confirm the compatibility of this specific caboxylate with PEG, but it would be worthwhile considering that the common copper alloy inhibitor, benzotriazole, is highly carcinogenic[631]. As discussed before, the bactericide effect of copper tends to allow only a thin layer of concretions on the surface of an artifact. One of the first treatment steps of a copper/waterlogged wood object is often to remove this concretion layer to enable chlorides to be easily released. Under concretion, copper alloy metal can be very well preserved. In this case, a sodium carboxylate might be adapted to prevent corrosion of the copper alloy while impregnating the wooden parts with PEG. Additionally, further tests on bare copper alloy samples would represent the surface of some copper alloy marine-recovered artifacts after removal of the concretions. The example given in section 5.1, of a copper alloy/waterlogged wood thermometer recovered from the USS *Monitor* could be an opportunity for further study. Again, further tests are needed to assess the effect of carboxylates on wood.

Hostacor IT® shows good results but its resistance to the accelerated aging was low. It protected however well bare and corroded carbon steel samples.

The case of the 20% (v/v) PEG 400/100ppm $NaNO_2$ mixture requires particular attention. Despite high $E_{corr}$ values, some of the bare coupons tarnished during immersion. The $E_{corr}$ values for corroded samples were slightly lower than with Hostacor IT®, but were still passivating. Also, if this corrosion inhibitor seems promising in PEG, its protective effect is limited (good $E_{corr}$ values but tarnishing of the samples). This limitation is probably due to the low pH of the solution. As mentioned in section 7.2, the low pH of this mixture is not fully understood[632]. A preliminary investigation suggested that the sodium

[628] Cook *et al.*, 1985, p.151.

[629] Hollner et al, 2007b, p.65; Rocca and Mirambet, 2007.

[630] Rocca and Mirambet, 2007, p.326.

[631] Scott, 2002, p.381.

[632] The pH of each solution separately is 6.6 (sodium nitrite) and 5.3 (PEG), but when added together, the pH decreased at 4.2.

nitrite could cause deprotonation of PEG, decreasing then the pH[633]. The exact reactions occurring require further research. However, this likely action of sodium nitrite on PEG suggests that these two chemicals are not compatible. Using this mixture on iron/waterlogged wood composites requires a pH increase of the solution to insure no attack of the metal or organic. Practical application would also assume that sodium nitrite is totally harmless to organics, but again, further research is needed. Thereby, a thorough study of sodium nitrite concerning its mode of action, its ability to reduce galvanic corrosion and its compatibility with PEG would be of great interest to conservation professionals.

They are several aspects of this study that could be improved upon. It would have been nice to have before and after pictures of the samples conditioned in the humidity chamber. As presented here, it was difficult to assess the effect of the humidity chamber on the coupons. Was corrosion due to corrosion in PEG or to humidity conditioning? Macro-photos of the surfaces, before and after the aging tests, could also have improved the interpretation of the results.

In addition, voltammetric plots of the samples in the solution of 20% (v/v) PEG 400/corrosion inhibitor could have described the reaction mechanisms in the mixture on the metal surfaces. These tests would have required more time and were therefore not possible within the framework of this diploma.

The analytical determination of the corrosion products from carboxylatation solution coupons could have enabled a better understanding of this inhibitive solution.

Lastly, it would have been interesting to assess the amount of PEG remaining at the surfaces of the samples after treatment. This would have allowed evaluating whether or not traces of PEG on the surface of the samples have an influence on their long term behavior. FTIR analyses would have been used for this purpose[634].

[633] Domjan, written communication, August 2008.

[634] FTIR (Fourrier Transformed Infra Red spectroscopy) is adapted to the analyses of organic compounds (Beck, 2006).

# 16. Conclusion

Non-separable iron/waterlogged wood artifacts recovered from a marine environment are complex objects requiring good knowledge of the conservation issues raised by both materials to be treated. It was first necessary to understand the burial environment and the degradation phenomena caused by it before approaching current conservation methods for both marine-recovered iron and waterlogged wood.

Besides the decay of each material, the degradation of iron/waterlogged wood objects creates chloride confinement zones at the interface iron/wood. Due to the manufacture and corrosion mechanisms of composites, it is not always possible to separate the components and gain access to these confinement zones.

Treating such artifacts requires compromises in order to adapt common conservation steps of both components to each other. Useful research in this field promoted notably electrolysis treatment, at neutral pH, to remove chlorides from the objects without damaging the wood with harsh alkaline solution.

However, a problematic treatment step for iron/waterlogged wood remains the impregnation of the wooden parts while insuring protection of the metal. The history of treatment proposals dealing with this issue has been discussed in detail (section 5.3). Apart the solvent based treatments adapted to small finds, it appeared that large iron/wood composites such as those of the *Monitor* have to be treated with another approach. The use of the corrosion inhibitor Hostacor IT® has been tested in PEG solutions for years to solve the PEG aggressiveness problem. However, several drawbacks of Hostacor IT® suggest that more studies are needed to optimize its use. Therefore, considering other corrosion inhibitors in acidic PEG solution was a worthwhile project to pursue.

Assessing the performances of corrosion inhibitors allowed a familiarization with common test methods used. Performing such trials also showed that reliable results can only be verified by measuring multiple samples. Therefore, this study should be considered as an initial investigation into potential treatments. A complete assessment into the effectiveness of corrosion inhibitors in PEG solutions should be performed by conservation scientists.

This study produced several interesting finds. The first is that, within the corrosion inhibitors considered (1% (v/v) Hostacor IT®, 100ppm $NaNO_2$, carboxylatation solution and 0.05M $NaC_{10}$), the sodium nitrite appeared to be the most suitable chemical to protect both bare and corroded metal surfaces in aqueous solution. Further study should be carried out to assess its effect on wood, but if sodium nitrite is harmless to organics, it could be a good alternative storage mixture for iron/waterlogged wood composites.

Another interesting result is that none of the corrosion inhibitor tested protected carbon steel samples enough to prevent further corrosion during a later immersion in 20% (v/v) PEG solution on its own.

Considering the corrosion inhibitors in 20% (v/v) PEG solution, the carboxylatation solution appeared not well suited to iron/wood composites. This mixture is too acidic and therefore not adapted to organics.

The sodium decanoate showed promising results on bare samples. The neutral pH of the $NaC_{10}$/PEG solution made it an interesting candidate for marine-recovered metal/wood composites. Nonetheless, the sodium decanoate itself does not protect corroded iron. Therefore, it may be useful to consider this family of corrosion inhibitors for copper/waterlogged wood artifact. As copper alloys can be very little corroded underwater, an adapted carboxylate, such as $NaC_7$, may be able to protect this metal during PEG impregnation of an attached wood component. Further research is necessary though, both on the compatibility of $NaC_7$ with PEG and on the impact of the carboxylate on wood.

The sodium nitrite solution also showed good results, but its compatibility with PEG may not be guaranteed. Indeed, the addition of 100ppm $NaNO_2$ in 20% (v/v) PEG significantly decreases the pH of the solution. This means, in the case of iron/wood objects, less protection of the metal and degradation of the wood due to the high acidity. Further research should be performed to better understand the PEG/sodium nitrite mixture and particularly why the pH becomes so low.

Considering these trials, Hostacor IT® remains the most suitable corrosion inhibitor, in PEG solution, due to its neutral pH and its propensity to passivate corroded steel. However, since this chemical is no longer being manufactured, further studies should seek and evaluate replacement chemicals for the preservation of non-separable iron/waterlogged wood artifacts. This corrosion inhibitor should be readily available, independent of a patent, easy to prepare, easy to use, affordable and safe.

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# *Figures*

## Note on illustrations

Information on the origin of the figures is given in the captions. If no source is mentioned, the figures were created by the author.

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# *Appendices*

## Appendix 1: Analysis of the metal samples: methods and results

The two metals tested during this study, bare and corroded, have been analyzed by X-Ray Fluorescence spectroscopy (XRF) with the apparatus at the Northrop Grumman Newport News's shipyard (VA). The same laboratory also performed optical emission spectroscopy (OES), to identify the steels according to AISI-SAE standards[635].

The corrosion products of a corroded sample have been analysed by X-Ray Diffraction (XRD).

Following is an overview of the techniques as well as the results.

### X-RAY FLUORESCENCE SPECTROSCOPY (XRF)

#### Technique description

The XRF method refers to two techniques: EDXRF and WXRF. In both cases, X-rays (primary photons) are applied to a sample, which then eject an electron from a material atom. This is followed by the reorganization of the atom's structure to a more stable state (electrons displacement). Through this displacement, electrons release energy in the form of X-ray fluorescence. This energy is transmitted to a spectrometer that processes the data and gives the elemental composition of a sample[636].

WXRF apparatus have an integrated crystal that diverge the X-ray beam. EDXRF is more common and does not require a sample preparation. EDXRF is often a complementary analysis system to scanning electron microscopy (SEM)[637].

#### XRF results

Bare metal

| Sample | Date | Cr | Mn | Ni | Mo | Cu | Si | Ti | V | Al |
|---|---|---|---|---|---|---|---|---|---|---|
| Iron | 02/05/08 09:38:38 AM | 0.04 | 0.43 | 0.00 | 0.01 | 0.00 | 0.05 | 0.00 | 0.00 | 0.05 |

| P | S | C | Co | As | Sb | Sn | Zr | Nb | Matrix(Fe) | Int(Cr) | Int(Mn) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.012 | 0.005 | 0.00 | 0.00 | 0.000 | 0.003 | 0.000 | 0.001 | 0.00 | 99.4 % | 2.8152 | 4.5602 |

| Int(Ni) | Int(Mo) | Int(Cu) | Int(Si) | Int(Ti) | Int(V) | Int(Al) | Int(P) | Int(S) | Int(C) |
|---|---|---|---|---|---|---|---|---|---|
| 0.9713 | 1.0461 | 1.2293 | 1.3872 | 1.0266 | 0.5590 | 1.0787 | 0.3485 | 0.1640 | |

| Int(Co) | Int(As) | Int(Sb) | Int(Sn) | Int(Zr) | Int(Nb) |
|---|---|---|---|---|---|
| 8.5731 | 0.9482 | 0.0273 | 1.8019 | 1.2031 | 1.3165 |

[635] AISI is the acronym for "American Iron and Steel Institute-Society of Automotive Engineers". SAE stand for the "Society of Automotive Engineers". See also chapter 7.1.

[636] Beck, 2006.

[637] *Ibid.*

Corroded metal

| Sample junkyard | Date | Cr | Mn | Ni | Mo | Cu | Si | Ti | V | Al |
|---|---|---|---|---|---|---|---|---|---|---|
| Corroded | 02/05/08 09:24:03 AM | 0.04 | 0.40 | 0.00 | 0.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.04 |

| P | S | C | Co | As | Sb | Sn | Zr | Nb | Matrix(Fe) | Int(Cr) | Int(Mn) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.012 | 0.005 | 0.00 | 0.00 | 0.000 | 0.003 | 0.008 | 0.002 | 0.00 | 99.4 % | 3.0486 | 4.2563 |

| Int(Ni) | Int(Mo) | Int(Cu) | Int(Si) | Int(Ti) | Int(V) | Int(Al) | Int(P) | Int(S) | Int(C) |
|---|---|---|---|---|---|---|---|---|---|
| 1.0827 | 1.0728 | 1.8030 | 0.6055 | 0.9576 | 0.4301 | 0.9050 | 0.3447 | 0.1795 | |

| Int(Co) | Int(As) | Int(Sb) | Int(Sn) | Int(Zr) | Int(Nb) |
|---|---|---|---|---|---|
| 8.6706 | 0.9581 | 0.0295 | 1.9409 | 1.2264 | 1.3238 |

## OPTICAL EMISSION SPECTROSCOPY (OES)

### Technique description

Optical (atomic) Emission Spectroscopy *"measures spectra emitted by atoms and ions with optical transitions in the wavelength range from about 100 nm to 900 nm. This range includes the ultraviolet, and visible light (from violet at 380 nm to red at 760 nm), and the near infra-red"*[638].

With OES, analyses can *"determine the chemical composition of solids, like steel or wood or paint, and liquids, like oil or milk, and gases, like air or car exhausts. Knowing the content of materials, we can monitor changes in the environment, and improve production processes and product properties, such as strength, corrosion resistance and appearance"*[639].

### OES results

Bare metal

2/5/2008 8:14:10 AM Sample: ~~ION~~ NON CORR
Type Standard: LAS Task: LAST

| Run | Cr | Mn | Ni | Mo | Cu | Si | Ti | V | Al | P | S | C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Avg | 0.0249 | 0.7883 | 0.0122 | 0.0067 | 0.0136 | 0.5112 | 0.0026 | 0.0684 | 0.0433 | 0.0262 | 0.0086 | 0.0892 |
| Sd | 0.0001 | 0.0008 | 0.0001 | 0.0000 | 0.0001 | 0.0014 | 0.0000 | 0.0001 | 0.0003 | 0.0002 | 0.0001 | 0.0003 |
| Sd% | 0.4600 | 0.0954 | 0.8065 | 0.6624 | 0.6853 | 0.2773 | 0.3352 | 0.1832 | 0.6047 | 0.6601 | 1.7306 | 0.2979 |

| | B | Zr | Pb | Sb | As | Sn | Nb | Co | FE% |
|---|---|---|---|---|---|---|---|---|---|
| Avg | -0.0008 | 0.0024 | 0.0000 | 0.0002 | 0.0019 | 0.0069 | 0.0012 | 0.0031 | 0.0000 |
| Sd | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0000 | 0.0001 | 0.0000 | 0.0000 | 0.0000 |
| Sd% | -1.3166 | 1.2766 | 0.0000 | 49.5445 | 1.0665 | 0.7597 | 0.7317 | 1.0462 | 0.0000 |

Corroded metal

2/5/2008 8:24:14 AM Sample: CORR. JNKYD
Type Standard: LAS Task: LAST

| Run | Cr | Mn | Ni | Mo | Cu | Si | Ti | V | Al | P | S | C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Avg | 0.0402 | 0.3794 | 0.0125 | 0.0037 | 0.0316 | 0.0088 | 0.0013 | 0.0012 | 0.0372 | 0.0110 | 0.0091 | 0.0674 |
| Sd | 0.0001 | 0.0014 | 0.0000 | 0.0001 | 0.0004 | 0.0002 | 0.0000 | 0.0001 | 0.0011 | 0.0001 | 0.0000 | 0.0005 |
| Sd% | 0.3407 | 0.3744 | 0.2943 | 3.7732 | 1.3869 | 2.5632 | 1.1630 | 4.2348 | 2.8634 | 1.0254 | 0.3589 | 0.7970 |

| | B | Zr | Pb | Sb | As | Sn | Nb | Co | FE% |
|---|---|---|---|---|---|---|---|---|---|
| Avg | -0.0009 | 0.0014 | 0.0000 | | 0.0020 | 0.0053 | 0.0006 | 0.0025 | 0.0000 |
| Sd | 0.0000 | 0.0001 | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0001 | 0.0001 | 0.0000 |
| Sd% | -0.7027 | 7.2667 | 0.0000 | -24.0092 | 0.2138 | 2.1390 | 17.1477 | 2.1553 | 0.0000 |

[638] Derzi and Lotito, 2007.

[639] *Ibid.*

Both metals are low alloy steel. The bare metal is a carbon steel type « 1011 » (AISI-SAE standards). The corroded samples were analyzed to and their AISI-SAE determination should be available soon.

The following table was provided by the shipyard scientists and represents the *"composition ranges and limits for AISI6SAE standard carbon steels containing less than 1.00% manganese – semifinished products for forging, hot rolled and cold finished bars, wire rod and seamless tubing"* (title of the table in the copy given). The ellipse correspond to the bare samples compositions.

| AISI-SAE designation | UNS designation | Heat composition ranges and limits, %(a) C | Mn | AISI-SAE designation | UNS designation | Heat composition ranges and limits, %(a) C | Mn | AISI-SAE designation | UNS designation | Heat composition ranges and limits, %(a) C | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1005 | G10050 | 0.06 max | 0.35 max | 1035 | G10350 | 0.32-0.38 | 0.60-0.90 | 1074(b) | G10740 | 0.70-0.80 | 0.50-0.80 |
| 1006 | G10060 | 0.08 max | 0.25-0.40 | 1037 | G10370 | 0.32-0.38 | 0.70-1.00 | 1075(b) | G10750 | 0.70-0.80 | 0.40-0.70 |
| 1008 | G10080 | 0.10 max | 0.30-0.50 | 1038 | G10380 | 0.35-0.42 | 0.60-0.90 | 1078 | G10780 | 0.72-0.85 | 0.30-0.60 |
| 1010 | G10100 | 0.08-0.13 | 0.30-0.60 | 1039 | G10390 | 0.37-0.44 | 0.70-1.00 | 1080 | G10800 | 0.75-0.88 | 0.60-0.90 |
| 1011(b) | G10110 | 0.08-0.13 | 0.60-0.90 | 1040 | G10400 | 0.37-0.44 | 0.60-0.90 | 1084 | G10840 | 0.80-0.93 | 0.60-0.90 |
| 1012 | G10120 | 0.10-0.15 | 0.30-0.60 | 1042 | G10420 | 0.40-0.47 | 0.60-0.90 | 1085(b) | G10850 | 0.80-0.93 | 0.70-1.00 |
| 1013(b) | G10130 | 0.11-0.16 | 0.50-0.80 | 1043 | G10430 | 0.40-0.47 | 0.70-1.00 | 1086 | G10860 | 0.80-0.93 | 0.30-0.50 |
| 1015 | G10150 | 0.13-0.18 | 0.30-0.60 | 1044 | G10440 | 0.43-0.50 | 0.30-0.60 | 1090 | G10900 | 0.85-0.98 | 0.60-0.90 |
| 1016 | G10160 | 0.13-0.18 | 0.60-0.90 | 1045 | G10450 | 0.43-0.50 | 0.60-0.90 | 1095 | G10950 | 0.90-1.03 | 0.30-0.50 |
| 1017 | G10170 | 0.15-0.20 | 0.30-0.60 | 1046 | G10460 | 0.43-0.50 | 0.70-1.00 | | | | |
| 1018 | G10180 | 0.15-0.20 | 0.60-0.90 | 1049 | G10490 | 0.46-0.53 | 0.60-0.90 | | | | |
| 1019 | G10190 | 0.15-0.20 | 0.70-1.00 | 1050 | G10500 | 0.48-0.55 | 0.60-0.90 | | | | |
| 1020 | G10200 | 0.18-0.23 | 0.30-0.60 | 1053 | G10530 | 0.48-0.55 | 0.70-1.00 | | | | |
| 1021 | G10210 | 0.18-0.23 | 0.60-0.90 | 1055 | G10550 | 0.50-0.60 | 0.60-0.90 | | | | |
| 1022 | G10220 | 0.18-0.23 | 0.70-1.00 | 1059(c) | G10590 | 0.55-0.65 | 0.50-0.80 | | | | |
| 1023 | G10230 | 0.20-0.25 | 0.30-0.60 | 1060 | G10600 | 0.55-0.65 | 0.60-0.90 | | | | |
| 1025 | G10250 | 0.22-0.28 | 0.30-0.60 | 1064 | G10640 | 0.60-0.70 | 0.50-0.80 | | | | |
| 1026 | G10260 | 0.22-0.28 | 0.60-0.90 | 1065 | G10650 | 0.60-0.70 | 0.60-0.90 | | | | |
| 1029 | G10290 | 0.25-0.31 | 0.60-0.90 | 1069(b) | G10690 | 0.65-0.75 | 0.40-0.70 | | | | |
| 1030 | G10300 | 0.28-0.34 | 0.60-0.90 | 1070 | G10700 | 0.65-0.75 | 0.60-0.90 | | | | |

(a) Limits on phosphorus and sulfur contents are given in Table 3; typical limits are 0.040% maximum phosphorus and 0.050% maximum sulfur. When silicon ranges or limits are required, the values in Table 3 apply. Steels listed in this table can be produced with additions of lead or boron. Leaded steels typically contain 0.15 to 0.35% lead and are identified by inserting the letter "L" in the designation—11L17; boron steels can be expected to contain 0.0005 to 0.003% boron and are identified by inserting the letter "B" in the designation—15B41. (b) SAE standard grade only. (c) AISI standard grade only.

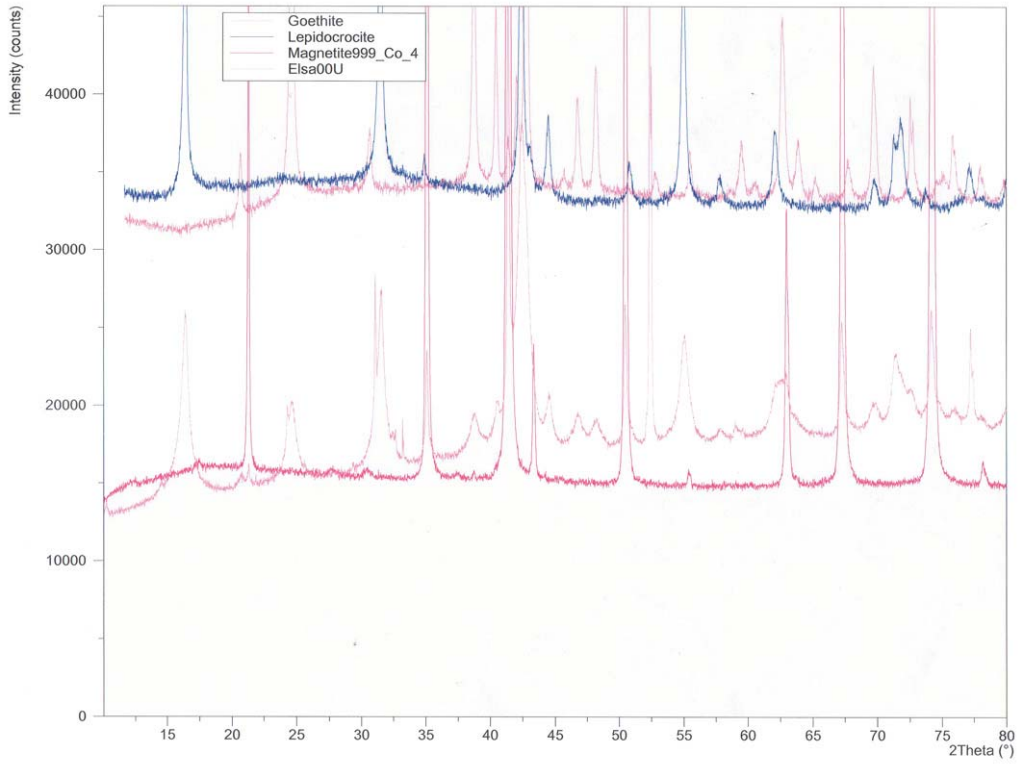
### X-RAY DIFFRACTION (XRD)

The XRD apparatus used to identify the corrosion products of a sample is located at the Physics Department of ODU, in Norfolk (VA). Dr. D.C. Cook proceeded to the analysis.

**Technique description**

XRD is a method used to identified nature and structure of crystallized products[640]. "*The atomic planes of a crystal cause an incident beam of X-rays (if wavelength is approximately the magnitude of the interatomic distance) to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction*"[641]. "*As an x-ray beam travels through any substance, its intensity decreases with the distance traveled through the substance*"[642].

**XRD results**




[640] Philippon, 1997.

[641] Glossary of Materials Science, 2000.

[642] X-ray Diffraction, 2000. For more details about the method, see Philippon, 1997.

## Appendix 2: Monitoring chloride removal from the analogue material

As mentioned in chapter 8.2.2, the chlorides release from a corroded sample over time was monitored. This was done to assess whether the sample contained significant chloride contamination that would require batch desalination. The sample was immersed in a 2% NaOH solution. A few drops of the solution were sampled and measured for chloride concentration. The results presented below were obtained with a chlorimeter. According to the low amount of chlorides in the solution after one week, it was decided that the corroded samples did not required a desalination treatment before starting the study.

-02/23/08
-Machine: Jenway PCLM3
-Standard: Alltech 200ppm open 02/08

Standard titration: 199ppm
Trial 1: 02/21/08: 6ppm
Trial 2: 02/21/08: 0ppm
Trial 3: 02/21/08: 1ppm
Trial 4: 02/21/08: 0ppm
Trial 5: 02/22/08: 8ppm

Standard titration: 203ppm
Trial 1: 02/22/08: 0ppm
Trial 2: 02/22/08: 7ppm
Trial 3: 02/22/08: 0ppm
Trial 4: 02/22/08: 0ppm
Trial 5: 02/22/08: 10ppm
Trial 6: 02/22/08: 1ppm

Standard titration: 208ppm
Trial 1: 02/23/08: 2ppm
Trial 2: 02/23/08: 0ppm
Trial 3: 02/23/08: 9ppm
Trial 4: 02/23/08: 0ppm
Trial 5: 02/23/08: 1ppm

-02/27/08
-Machine Jenway PCLM3
-Standard: Alltech 200ppm open 02/08

Standard titration: 201ppm
Trial 1: 02/24/08: 0ppm
Trial 2: 02/24/08: 7ppm
Trial 3: 02/24/08: 3ppm
Trial 4: 02/24/08: 7ppm
Trial 5: 02/24/08: 1ppm
Trial 6: 02/24/08: 0ppm

Standard titration: 207ppm
Trial 1: 02/25/08: 1ppm
Trial 2: 02/25/08: 0ppm
Trial 3: 02/25/08: 10ppm
Trial 4: 02/25/08: 1ppm
Trial 5: 02/26/08: 12ppm
Trial 6: 02/26/08: 1ppm

Standard titration: 202ppm
Trial 1: 02/26/08: 9ppm
Trial 2: 02/26/08: 8ppm
Trial 3: 02/27/08: 8ppm
Trial 4: 02/27/08: 11ppm
Trial 5: 02/27/08: 1ppm
Trial 6: 02/27/08: 1ppm

# Appendice 3: Material and suppliers

- Ethanol.....INDUSTRIAL CHEMICALS
- Epoxy.....EPOXY SYSTEMS
- Jars, Glass body Ag-AgCl Reference Electrodes, Compact Multimeters, Sodium nitrite, Carboxylic acid, Hydrogen peroxide, Gloves, Mask, Parafilm M®, pH-meter, Oven, Silica gel..... FISHER SCIENTIFIC
- Banana plugs, Crocodile plugs, Wires.....RADIO SHACK
- Grips.....ACE HARDWARE
- PEG.....SPECTRUM LABORATORY SERVICES
- Chlorides analysis..... JENWAY
- Polishing machine.....BUEHLER
- Potentiostat.....AMETEK PRINCETON APPLIED RESEARCH

## SUPPLIER / MANUFACTURER DETAILS

| | | | |
|---|---|---|---|
| ➢ Ace Peninsula Hardware | 12490 Warwick Blvd,<br>Newport news, VA, 23606 | | 1-757-594-9890 |
| ➢ AMETEK Princeton Applied Research | 801 South Illinois Avenue<br>Oak Ridge, TN U.S.A | | 1-865-482-4411<br>1-865-483-2279 |
| ➢ Buehler | 41 Waukegan Rd. P.O. Box 1<br>Lake Bluff, IL 60044-1699 • USA | | 1-847-295-6500<br>1-847-295-7979 |
| ➢ Epoxy System | Florida & Vermont, info@epoxy.com<br>www.epoxy.com | | 1-352-489-1666<br>1-352-465- 3497 |
| ➢ Fisher Scientific | www.fishersci.com | | 1-800-766-7000<br>1-800-926-1166 |
| ➢ Industrial Chemicals | 2540 Bellwood Road<br>Richmond, VA, 23237 | webmaster@industrialchemicals.com | |
| ➢ Jenway (Bibby Scientific T/As Jenway) | Gransmore Green<br>Felsted, Dunmow<br>Essex, ENGLAND | | 0044(0)1371-820122<br>0044(0)1371-821083 |
| ➢ Radio Shack | 12300 Jefferson Avenue<br># C-9, Newport News, VA 23602 | | 032/ 926 90 51 |

| | | |
|---|---|---|
| ➢ Spectrum Laboratory Services | 14422 So. San Pedro Street | 1-310-516-8000 |
| | Gardena, CA 90248 | 1-310-516-8000 |

## Appendix 4: Samples dedicated to voltammetry and to the humidity chamber

#### ORGANIZATION OF THE VOLTAMMETRIC ANALYSES

Previously untreated samples (reference samples):

- 3 bare samples in 70% PEG without previous $E_{corr}$ monitoring
- 3 bare samples in 70% PEG with $E_{corr}$ monitoring
- 5 corroded samples in 70% PEG without previous $E_{corr}$ monitoring
- 3 corroded samples in 70% PEG with $E_{corr}$ monitoring (not enough samples foresee to run 5)

For one third of the one-step treatment samples (see also sketch next page), $E_{corr}$ monitoring was performed in 70% PEG before polarization. To review, the one-step treatment samples were:

- 8 samples pretreated with 20%PEG+Hostacor IT®
    - 1 bare sample in 70% PEG with $E_{corr}$ monitoring
    - 2 bare samples in 70% PEG without $E_{corr}$ monitoring
    - 2 corroded samples in 70% PEG with $E_{corr}$ monitoring
    - 3 corroded samples in 70% PEG without $E_{corr}$ monitoring
- 8 samples pretreated with 20%PEG+$NaNO_2$
    - 1 bare sample in 70% PEG with $E_{corr}$ monitoring
    - 2 bare samples in 70% PEG without $E_{corr}$ monitoring
    - 2 corroded samples in 70% PEG with $E_{corr}$ monitoring
    - 3 corroded samples in 70% PEG without $E_{corr}$ monitoring
- 8 samples pretreated with 20%PEG+carboxylatation solution
    - 1 bare sample in 70% PEG with $E_{corr}$ monitoring
    - 2 bare samples in 70% PEG without $E_{corr}$ monitoring
    - 2 corroded samples in 70% PEG with $E_{corr}$ monitoring
    - 3 corroded samples in 70% PEG without $E_{corr}$ monitoring
- 3 samples pretreated with 20%PEG+$NaC_{10}$
    - 1 bare sample in 70% PEG with $E_{corr}$ monitoring
    - 2 bare samples in 70% PEG without $E_{corr}$ monitoring

**SKETCH SHOWING SAMPLES CONDITIONING GROUPS FOR VOLTAMMETRY AND HUMIDITY CHAMBER**

In regards to voltammetric trials, samples mentioned above are part of the following diagram excluding the "Previously untreated samples" that were extra samples.